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An Optical Lever Manometer. J. E. SHRADER and E. M. RYDER 321
The Logarithmic Law Connecting Atomic Number and Frequency Differences in Spectral Series. GLADYS A. ANSLOW 326
On the Characteristics of Electrically Operated Tuning Forks. H. M. DADOURIAN 327
The Mathematical Structure of Band Series, II. RAYMOND T. BIRGE 361
The Passage of Photoelectrons Through Metals. K. T. Compton and L. W. ROGS 374
New Books. 399

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Second Series *May, 1919* *Vol. XIII., No. 5*

THE

PHYSICAL REVIEW.

AN OPTICAL LEVER MANOMETER.

By J. E. Shrader and H. M. Ryder.

Synopsis.—To meet the demand for a gauge which will measure vapor pressures in the range between that which can be measured by the Knudsen Gage (.001 mm.) and the ordinary mercury manometer, a new type of gage has been devised. This consists of a rather large mercury manometer in one arm of which a small optical lever is so adjusted that it measures small changes in level due to differences of pressure. The range of the instrument for accurate work is from .001 mm. to 3 or 4 mm. The instrument can also be used as a differential gage with the same accuracy. In use the changes in pressure can be observed by the deflection of a beam of light and may be recorded by a photographic device. Curves are given from a photographic record of the action of the gage during the release of CO_2 and water vapor which had been frozen out in a trap with liquid air. Attention is called to the rapidity with which this gage responds to changes of pressure.

THE McLeod gage has long served as a means of measuring pressures of several millimeters or mercury down to the order of 10^{-5} mm. There are two fundamental cases, however, to which this gage is not applicable in this range, that is, when vapors are to be measured, and where there is a rapidly changing pressure to be recorded. In the first of these cases the McLeod gage becomes useless, due to the fact that Boyle's Law is not applicable to vapors. In the second case the McLeod gage, in its most favorable form, may be much too slow moving, and has no recording feature.

At the present time, when many pumps are on the market which enable more or less leaky systems to be maintained at low pressures, it has become desirable to determine accurately vapor pressure of many substances at pressures below those usually recorded. One of the writers[1] has reported a method of obtaining low vapor pressures accurately, which in a simplified and refined form is capable of operation down to the lower limits of the McLeod gage, but which is applicable to only a certain class of substances, namely those which can be distilled within range of tem-

[1] Ryder, Journal Franklin Institute, Vol. 186, No. 1, July, 1918.

peratures available in the laboratory for such work, and which is not suitable for rapid determinations. The ability to observe rapidly changing pressures, or to record them, would mean, too, the facilitating of a number of operations in the laboratory or shop.

One of the writers[1] has given a preliminary report of a gage designed to provide for the particular requirements suggested in the foregoing. It is the object of this paper to describe the essential details of this gage, and to give a few examples of its actual performance.

The principle of this gage is shown in Fig. 1. A mercury U-tube manometer is formed in the usual manner, except that the surfaces of the mercury are so arranged as to be of relatively large area. Above one

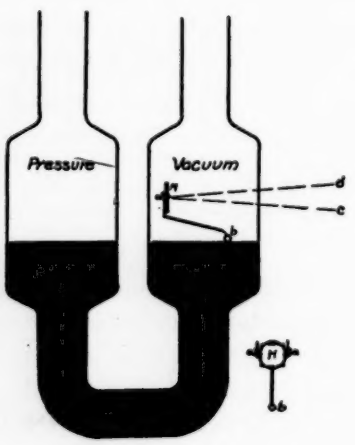

Fig. 1.
Optical Lever Manometer.

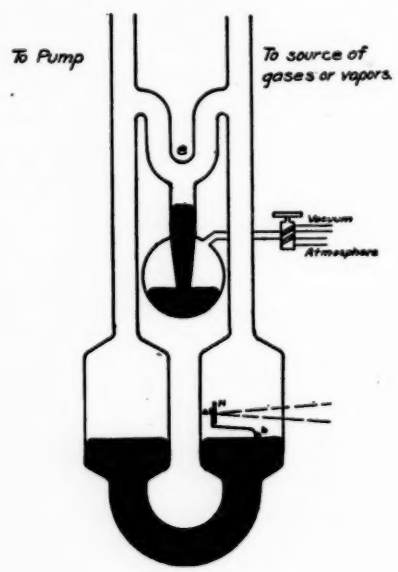

Fig. 2.
System for Manometer.

of the surfaces, within the tube, is arranged an optical lever, as shown in the figure. This lever is supported by two knife edges, *a*–*a*, which rest on loops of wire, which in turn are sealed into the glass walls of the tube, a glass bead *b*, fused to the end of the lever arm acts as a float on the mercury surface, and in this way transmits the motion of the mercury surface to the lever arm. A mirror *M* attached at the position shown acts in the usual manner to reflect a beam of light from the lamp *c* to the scale *d*, if the gage is to be arranged as an indicating instrument. If the gage is to be used for recording variations in pressure, the scale may be replaced by a photographic device such as is used in oscillographic work.

[1] Shrader, Pittsburgh Meeting, American Physical Society, December, 1917.

Fig. 2 shows a convenient method for connecting this gage in a system. The cross connection *e* provides an easy means of evacuating the whole system with one pump located as shown. With this stop-cock or mercury cutoff open, a zero reading can be easily obtained, after which this connection may be closed and the gases or vapors introduced for measurement. This system provides also for the measurement of small variations in pressure, with an original pressure of any desired value, this value in no way affecting the absolute sensibility of the gage.

The gage as shown is a primary instrument, since the pressure corresponding to any deflection on the scale may be calculated from dimensions which may be readily determined. The lowest pressure which may

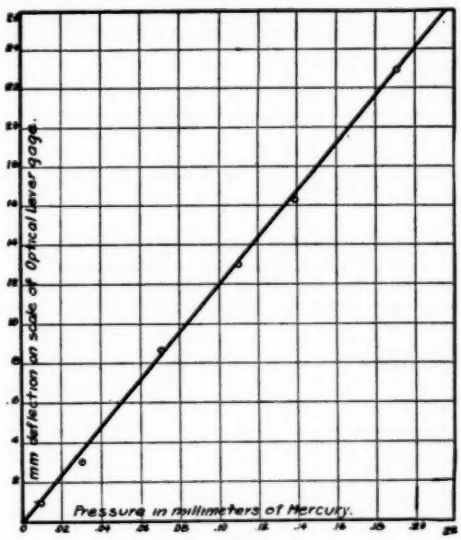

Fig. 3.

Calibration curve for an Optical Lever Gage.

be observed with the gage is that which gives the minimum appreciable movement of the mercury, and has been determined by experience to be approximately one thousandth of a millimeter of mercury in a properly designed gage. The upper limit, is, of course, determined by the dimensions of the gage, and is easily made to overlap the lower accurate readings of an ordinary U-tube manometer. The only source of error which need be considered is that due to the adhesion of the mercury to the walls of the tube, the deflection being therefore less than the actual value. If the mercury is very clean, and the glass in good condition a large mercury surface reduces this error to a negligible quantity. Mercury surfaces of from 5 cm. to 10 cm. diameter are in use. Some gages

have had a window of plane glass at the point of transmission through the tube of the beams of light, to prevent any possibility of a refraction of the beams due to the curvature of the glass.

Fig. 3 shows a check curve plotted between scale readings of this "optical lever" gage as ordinate and the actual pressures, as measured by a McLeod gage (hydrogen being the gas used). It will be seen that with this gage, up to the limit of this curve, .2 mm., a straight line relation exists. Above this point, the line is slightly curved, due to the flat scale used, and to the angular movement of the lever arm. This curve shows, too, the variations from the true value which may be expected from consecutive readings. The relative variation of this curve from its calculated position depends principally on the accuracy of the calculation. A convenient method of obtaining accurately the lever arm ratio consists in mounting the lever in a vessel of known cross sectional area

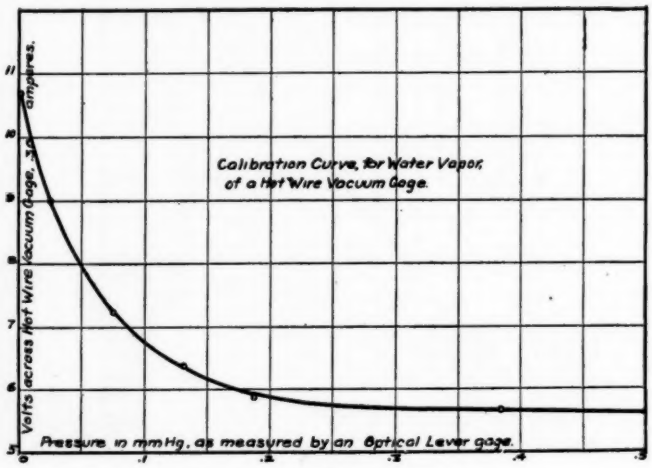
Volts across Hot Wire Vacuum Gage. .30 amperes.
Calibration Curve, for Water Vapor, of a Hot Wire Vacuum Gage.
Pressure in mm Hg. as measured by an Optical Lever gage.

Fig. 4.

Use of Optical Lever Gage as a Primary Instrument.

with the float resting on mercury, in its normal position. When small known amounts of mercury are added, the movement of the beam of light on a properly placed scale may be observed, and the lever arm ratio calculated.

By means of this gage as a primary instrument the use of the hot wire gage[1] may be extended to the measurement of vapor pressures. Fig. 4 is a calibration curve for the hot wire gage for water vapor, the pressure being determined by the "optical lever" gage.

Fig. 5 is a reproduction of a graphic chart obtained by using the

[1] Pirani, Verh. I. Deutsch Phys. Gesell., 24, p. 686, 1906.

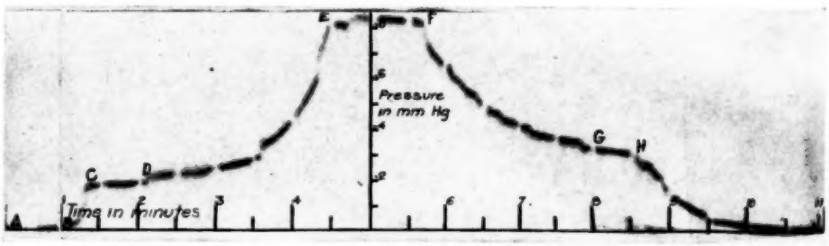

Fig. 5.

J. E. SHRADER AND H. M. RYDER.

"Optical lever gage." The apparatus used was that shown in Fig. 2 with the addition of a tube arranged for immersing in liquid air, connected to the right leg of the U-tube. At the point *A* on the chart, all gases have been removed from the system except some water vapor and CO_2 which are held frozen in the tube immersed in liquid air. With the cross connection closed, the liquid air is removed. At *B* active vaporizing starts. At *C* the CO_2 has been released, at *D* water vapor is coming off, and at *E* this vaporization is complete. At *F* solid CO_2 is applied and the water starts to freeze out again, this freezing out becoming complete at *G*. At *H* the solid CO_2 is replaced by liquid air and freezing out of the CO_2 begins. This is completed at *J*, the gage being thus brought back to zero reading. This chart is shown merely to give an idea of the possibilities of the "optical lever" gage in this direction. Many problems of diffusion, gas evolution, etc., immediately present themselves for solution with the aid of this device.

Some idea of the maximum rapidity of pressure variation which the optical lever gage will record may be gained from Fig. 6 which shows a

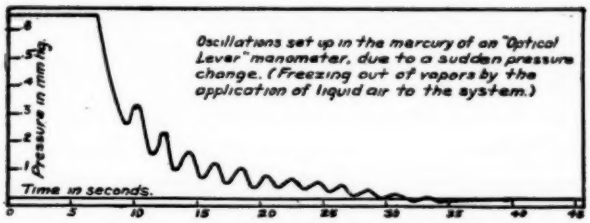
Oscillations set up in the mercury of an "Optical Lever" manometer, due to a sudden pressure change. (Freezing out of vapors by the application of liquid air to the system.)
Pressure in mm Hg.
Time in seconds.

Fig. 6.

record of the freezing out of water vapor by means of liquid air. The oscillations are due to the original sudden pressure drop, and have a period of slightly more than two seconds (approximately 1,000 grams of mercury in the gage). The design of the gage may be such that this period may be materially reduced.

To summarize, a primary vacuum gage, consisting of the optical lever principle applied to a mercury U-tube manometer has been devised for indicating or recording pressures, including pressure variations, of vapors as well as gases, the pressure range being from several millimeters of mercury to approximately one thousandth of a millimeter. All errors of any consequence may be eliminated. By the use of this gage with the addition of a standard photographic device, charts may be obtained showing accurately pressure changes due to such phenomena as vaporization, freezing, diffusion, etc.

WESTINGHOUSE RESEARCH LABORATORY,
EAST PITTSBURGH, PA.,
January, 1919.

THE LOGARITHMIC LAW CONNECTING ATOMIC NUMBER AND FREQUENCY DIFFERENCES IN SPECTRAL SERIES.

By Gladys A. Anslow.

Synopsis.—In continuation of a previous note by Anslow and Howell graphic and algebraic relations are derived between the logarithms of the atomic numbers and of the ν, $\nu_1 + \nu_2$, ν_1 and ν_2 constant frequency differences occurring in the spectral series of alternate members of the same chemical family. Two systems of four approximately straight lines approaching parallelism resulted when a family possessed both doublet and triplet series. The equations derived are of the form $\nu = (N/mnk)^A$, where N is the atomic number of the element; A is a constant depending upon the system; n is an integer, the same for both systems in the same family; k is a constant, 0.080; and m takes on successive integral values for the ν, $\nu_1 + \nu_2$, and ν_1 equations. The agreement between the calculated and observed values of frequency differences indicates that the logarithmic lines should curve upwards for elements of high atomic number. The equations derived and the fact that an approximate linear relation seems to exist between the convergence frequencies of members of the same system of series and their atomic numbers do not seem to follow from the Bohr-Sommerfeld theory of atomic structure as so far developed and indicate that some adjustments to the theory are necessary if it is to be extended to predict optical series.

IN an earlier note Mrs. Janet Howell Clark and the author[1] called attention to an extension of the modified law of Runge and Precht[2] concerning the frequency differences of the doublet and triplet spectral series in a given family of the Mendelejeff chemical series. Ives and Stuhlmann[3] had found by a graphical method that a linear relation exists between the logarithms of the atomic numbers of the elements of one family and the logarithms of their doublet separations. Plotting the logarithms of the atomic numbers of the members of the second chemical family against the logarithms of the sum of the constant frequency differences of the triplets in their spectra, we found that linear relations exist between alternate members of the family, the points for magnesium, zinc, cadmium and mercury lying on one line, and those for calcium, strontium, barium and radium on another.

Bell[4] has recently published a treatise on the relation of atomic number to the doublet and triplet separations in the different chemical families. Testing the relation $\nu = A(N - N_0)^2$, where ν stands for the frequency

[1] Anslow and Howell, Proceedings of the National Academy of Sciences; III., p. 409, 1917.
[2] Runge and Precht, Philosophical Magazine; V., p. 476, 1903.
[3] Ives and Stuhlmann, Phys. Rev., V., p. 368, 1915.
[4] Bell, Philosophical Magazine, XXXVI., p. 337, 1918.

difference, N for the atomic number, and A and N_0 are constants, he finds that such an equation approximately predicts the doublet and triplet separations of the different elements if we assume two such

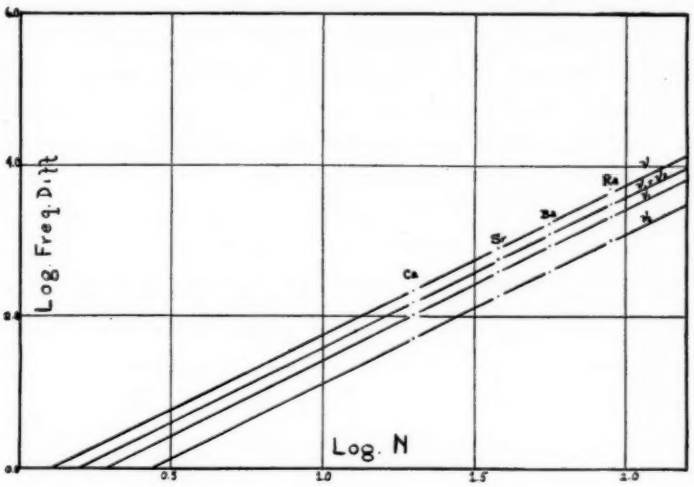

Fig. 1.

equations for each family which branch in the case of the first and second families at potassium and magnesium respectively. He also derives an equation for the logarithmic relation between the same quantities, putting

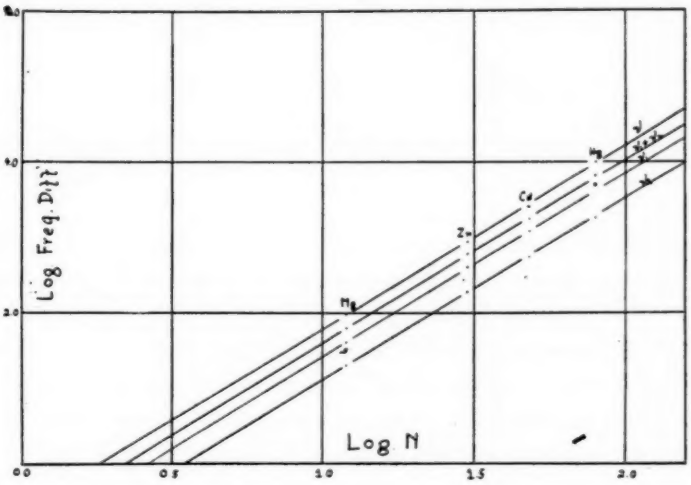

Fig. 2.

the equation in the form, $\log \nu = p \log N + q$, where p and q are constants, but discards such a relation as not an essential improvement

upon the relation $\nu = A(N - N_0)^2$. He also states that "the logarithmic method fails to show graphically the branching relation of the columns."

However, the plotting of the logarithmic equations does show the existence of two equations for each family as is evident from the diagrams in the article by Mrs. Clark and myself, where we attempted to make this fact clear. It happens that I had calculated the equations of the logarithmic lines for the different families where series are known and since the form in which I stated my final results is slightly different from Mr. Bell's, it shows some interesting relationships.

Since the spectral series of the elements in the second chemical family have been the most fully worked out for any family, I will consider it first. I have plotted the logarithms of the doublet separation, ν, and of the triplet separations ν_1, ν_2, and $\nu_1 + \nu_2$ against the logarithms of the

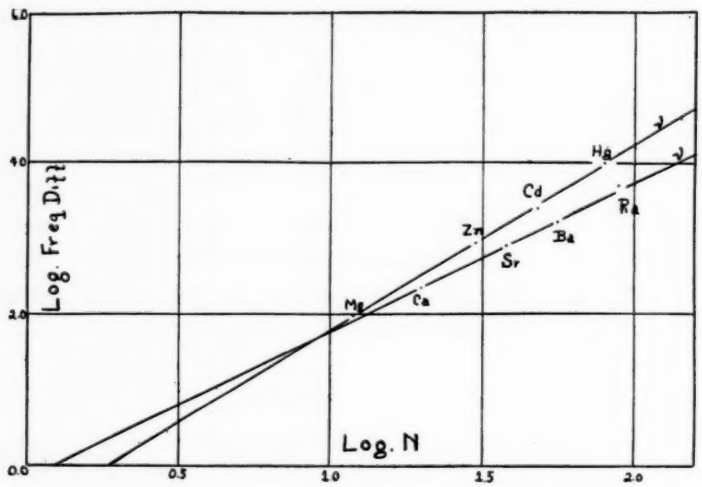

Fig. 3.

atomic numbers of the elements and have obtained lines which pass through Ca, Sr, Ba and Ra (Fig. 1), and through Mg, Zn, Cd and Hg (Fig. 2). The striking feature of the result is that the lines for each system are approximately parallel. If the two systems are plotted on the same diagram, corresponding lines will intersect at points slightly below those for magnesium. This fact is shown for the ν lines in Fig. 3. The equations of the lines were first put into the form,

$$\log \nu = A(\log N - C)$$

and this equation then solved into $\nu = (N/B)^A$, where B = antilog. C. The constants A and B which appear in the mean equations of the lines are tabulated below.

The values for the frequency differences are taken, for the sake of comparison, the same as those taken by Bell and given by Dunz.[1] The values for the radium triplets are those given in our earlier paper. It should be noticed that the triplet differences 2050 and 832 found by Hicks[2] fit almost as well into the equations derived. Values marked * were not used in the calculation of the formulæ.

TABLE I.

Element.	N.	ν Obs.	ν Calc.	ν Calc.$-\nu$ Obs.	$\nu_1+\nu_2$ Obs.	$\nu_1+\nu_2$ Calc.	$\nu_1+\nu_2$ Calc. $-\nu_1+\nu_2$ Obs.
Ca.....	20	222.9	225.6	+ 2.7	158.10	159.8	+ 1.7
Sr.....	38	801.3	795.8	− 5.5	581.49	578.0	+ 3.5
Ba.....	56	1690.5	1704.6	+ 14.1	1248.7	1255.6	+ 6.9
Ra.....	88	4858.0*	4140.9	−717.1	3052.7*	3103.9	+ 51.2
	A = 1.964 B = 1.267 = 4 × .317				A = 2.002 B = 1.586 = 5 × .317		
Element.	N.	ν_1 Obs.	ν_1 Calc.	ν_1 Calc. $-\nu_1$ Obs.	ν_2 Obs.	ν_2 Calc.	ν_2 Calc. $-\nu_2$ Obs.
Ca.....	20	105.99	105.5	− 0.5	52.11	52.1	+ 0.0
Sr.....	38	394.44	394.7	+ 0.3	187.05	187.0	+ 0.0
Ba.....	56	878.4	875.6	− 2.8	370.3*	408.4	+ 38.1
Ra.....	88	2016.6*	2216.6	+200.0	1036.1*	1005.8	− 30.3
	A = 2.055 B = 2.072 = 6 × .345				A = 1.994 B = 2.747		
Element.	N.	ν Obs.	ν Calc.	ν Calc. $-\nu$ Obs.	$\nu_1+\nu_2$ Obs.	$\nu_1+\nu_2$ Calc.	$\nu_1+\nu_2$ Calc. $-\nu_1+\nu_2$ Obs.
Mg.....	12	92.0	91.4	− 0.6	60.86	61.0	+ 0.1
Zn.....	30	872.4	872.6	+ 0.2	578.79	578.1	− 0.8
Cd.....	48	2484.1*	2776.4	+312.3	1712.91*	1831.7	+118.8
Hg.....	80	9835.06	9766.2	− 68.9	6397.50	6412.2	+ 14.7
	A = 2.462 B = 1.917 = 6 × .319				A = 2.454 B = 2.247 = 7 × .321		
Element.	N.	ν_1 Obs.	ν_1 Calc.	ν_1 Calc. $-\nu_1$ Obs.	ν_2 Obs.	ν_2 Calc.	ν_2 Calc. $-\nu_2$ Obs.
Mg.....	12	40.95	40.9	+ 0.0	19.89	19.9	+ 0.0
Zn.....	30	388.91	388.9	+ 0.0	189.78	189.8	+ 0.0
Cd.....	48	1171.05*	1234.1	+ 63.0	541.86*	604.2	+ 63.3
Hg.....	80	4630.31*	4328.4	−301.9	1767.19*	2127.0	+359.8
	A = 2.457 B = 2.648 = 8 × .331				A = 2.462 B = 3.560		

The equations derived show that A is approximately constant for each system, as is to be expected since the plotted lines approach parallelism. Moreover, the constants B for the ν, $\nu_1 + \nu_2$ and ν_1 lines of

[1] Dunz, Bearbeitung unserer Kentnisse von der Serien, Tubingen, 1911.

[2] Hicks, Philosophical Transactions, A, CCXIL., 33.

both systems are successive integral multiples of the same factor, 0.32. The agreement between the observed and calculated values for the separations is fairly good for elements of low atomic number, but poor for those elements which lie beyond the rare earths in the chemical series. The differences between the values found for cadmium seem to indicate that either the series used are not related to those with which they are commonly supposed to be similar to in other elements, or the structure of the atom of this element is not exactly similar to that of the other elements in the same group, so that it acts as if its atomic number were less than that which has been assigned to it. Attention is also called to the fact that much better values could be calculated for the ν_1 separations of radium and mercury if the values of B were more nearly equal to $6 \times .320$ and $8 \times .320$, respectively.

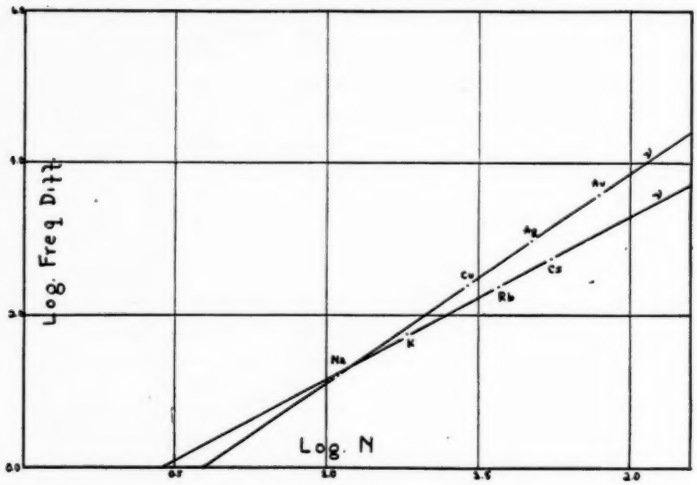

Fig. 4.

Since alternate elements are related in this way, it should be possible to predict frequency differences in elements where they are not yet known. The lines through Ca, Sr, Ba and Ra predict the separations $\nu = 9.56$; $\nu_1 + \nu_2 = 6.95$; $\nu_1 = 3.91$; and $\nu_2 = 2.17$ for beryllium. The spectrum shows the differences 8.9, 6.8, 4.1 and 2.5 between lines which occur in pairs, but not in triplets. A magnetic study of the lines in question has been made by Popow[1] proving that they belong to doublet and triplet series. Possibly the simplicity of the atom prevents the appearance of the three lines in the spectrum at once, but permits doublets with the separations corresponding to the triplet separations.

The results for Group I are plotted in Fig. 4 and the equations derived

[1] Popow, Verhandlungen der Schweizerischen Naturforschenden Gesellschaft, Sept., 1913.

are shown in Table II. In this group only the doublet series have been discovered with the exception of copper.

TABLE II.

Element.	N.	ν Obs.	ν Calc.	ν Calc. − ν Obs.	Element.	N.	ν Obs.	ν Calc.	ν Calc. − ν Obs.
Na.....	11	17.21	17.21	+0.0	Li.....	3	0.34*	1.09	+0.7
Cu.....	29	248.13*	245.4	−2.7	K.....	19	57.90	57.1	−0.8
Ag.....	48	920.56	922.0	+1.4	Rb.....	37	237.71	239.0	+1.3
Au.....	79	3817.20	3826.7	+9.5	Cs.....	55	564.10	559.7	−4.4
$A = 2.741$ $B = 3.895 = 8 \times .486$					$A = 2.147$ $B = 2.887 = 6 \times .481$				

As in Group 2 two values appear for A, and B is seen to be an integral multiple of the constant, 0.483. If the behavior of the light emitting electrons of the two families is similar, we should expect the appearance of triplet series in this group, and the equations which should predict the values of $\nu_1 + \nu_2$ and ν_1 are for Na, Cu, Ag and Au

$$\nu_1 + \nu_2 = \left(\frac{N}{9 \times .483}\right)^{2.741}$$

and

$$\nu_1 = \left(\frac{N}{10 \times .483}\right)^{2.741};$$

and for Li, K, Rb and Cs

$$\nu_1 + \nu_2 = \left(\frac{N}{7 \times .483}\right)^{2.147}$$

and

$$\nu_1 = \left(\frac{N}{8 \times .483}\right)^{2.147}.$$

Two systems of triplets have been discovered in the spectrum of copper by Rydberg[1] with the separations $\nu_1 + \nu_2 = 129.50 + 50.58 = 180.08$; and $680.10 + 212.21 = 892.41$. Assuming that A should have the same value for these triplets as for the doublets the values derived for B are

$B^{\nu_1+\nu_2}$,	$4.324 = 9 \times .481$;	$2.432 = 10 \times .243$
B^{ν_1},	$4.918 = 10 \times .491$;	$2.685 = 11 \times .244$
B^{ν_2},	6.728	4.102

The agreement between the predicted values for B and those derived from the triplets with the smaller frequency differences is striking, the other system of triplets being, apparently, a secondary one with B a

[1] Rydberg, Astrophysical Journal, VI., p. 239, 1897.

multiple of a constant half as large as for the other. These results support the hypothesis that the graphs for the ν, $\nu_1 + \nu_2$, ν_1, and ν_2 separations in Figs. 1 and 2 are parallel straight lines.

If the latter three lines are parallel, the following equations can be stated for the triplets in any element

$$\nu_1 + \nu_2 = \left(\frac{N}{B_{\nu_1+\nu_2}}\right)^A \tag{1}$$

$$\nu_1 = \left(\frac{N}{B_{\nu_1}}\right)^A \tag{2}$$

$$\nu_2 = \left(\frac{N}{B_{\nu_2}}\right)^A \tag{3}$$

and subtracting (2) from (1)

$$\nu_2 = (N)^A\left[\left(\frac{1}{B_{\nu_1+\nu_2}}\right)^A - \left(\frac{1}{B_{\nu_1}}\right)^A\right] \tag{4}$$

which leads to the following relation between the constants,

$$\left[\left(\frac{1}{B_{\nu_1+\nu_2}}\right)^A - \left(\frac{1}{B_{\nu_1}}\right)^A\right]^{1/A} = \frac{1}{B_{\nu_2}}. \tag{5}$$

I have tested this result for the triplets considered. The ν_1 value for A for Ca, Sr, Ba, and Ra is so different from those for $\nu_1 + \nu_2$ and ν_1 that I have calculated second values for B from the Ca, Sr and Ba ν_1 separations, and from the Ca and Sr ν_2 separations, assuming $A = 2.002$, which is that derived for the $\nu_1 + \nu_2$ separations. The results are placed below those taken from Table I.

TABLE III.

System.	$B_{\nu_1+\nu_2}$.	B_{ν_1}.	$[(B^{-1}_{\nu_1+\nu_2})^A - (B^{-1}_{\nu_1})^A]^{-1/A}$.	B_{ν_2}.	$d(B_\nu)$.
Ca, Sr, Ba, Ra....	1.586	2.054	2.494	2.746	0.252
Ca, Sr, Ba, Ra....		1.922	2.800	2.780	0.020
Mg, Zn, Cd, Hg...	2.247	2.648	3.543	3.560	0.017
Cu.....	4.324	4.918	6.728	6.930	0.202
Cu.....	2.432	2.685	4.102	4.108	0.006

The values in the last column give the differences between the two calculated values of B_{ν_2}, and are so small that the hypothesis of parallelism between the series separations is strengthened.

Triplets appear again in Group VI., and have been discovered in the spectra of O, S and Se (Fig. 5). If the alternate members in this group are spectroscopically related those in O should not be related to those in

S and Se, but to the undiscovered triplets in Cr, Mo, W and U. From the separations $\nu_1 + \nu_2 = 18.15 + 11.13 = 29.16$ in S, and $\nu_1 + \nu_2 = 103.7 + 44.07 = 148.48$ in Se, the following equation is derived.

$$\nu_1 + \nu_2 = \left(\frac{N}{3.356}\right)^{2.160} = \left(\frac{N}{7 \times .479}\right)^{2.160}.$$

The similarity between this equation and the one predicted for the undiscovered triplets of Li, K, Rb and Cs is apparent. If they are identical

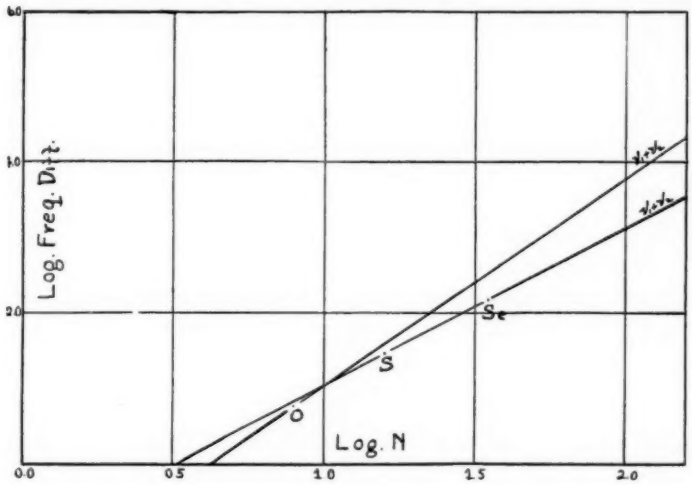

Fig. 5.

ν_1 and ν_2 should be given by parallel equations with $B = 8 \times .479$, and

$$B = \left[\left\{\left(\frac{1}{7}\right)^{2.160} - \left(\frac{1}{8}\right)^{2.160}\right\}\left(\frac{1}{.479}\right)^{2.160}\right]^{-1/2.160}.$$

These values give

$$\nu_1 + \nu_2 = 21.12 + 7.27 = 28.39 \text{ for S,}$$

and $111.63 + 37.04 = 148.67$ for Se. Better agreement would have been obtained if the values for B predicted for Li, K, Rb and Cs had been used.

The analogy suggests that the triplets in O may be given by the equations derived from the triplets in copper. Using these equations we obtain $\nu_1 + \nu_2 = 5.43$; $\nu_1 = 3.80$; and $\nu_2 = 1.61$. The observed differences as given by Runge and Paschen[1] are $3.70 + 2.08 = 5.78$.

The only other group where series of the first type have been worked out, with the exception of those in manganese, is in the third, where

[1] Runge and Paschen, Annalen der Physik, LXI., p. 641, 1897; Astrophysical Journal, VIII., p. 70, 1898.

doublets occur. The graph is shown in Fig. 6. The values of the constants derived from the frequency differences which are known are shown in Table IV.

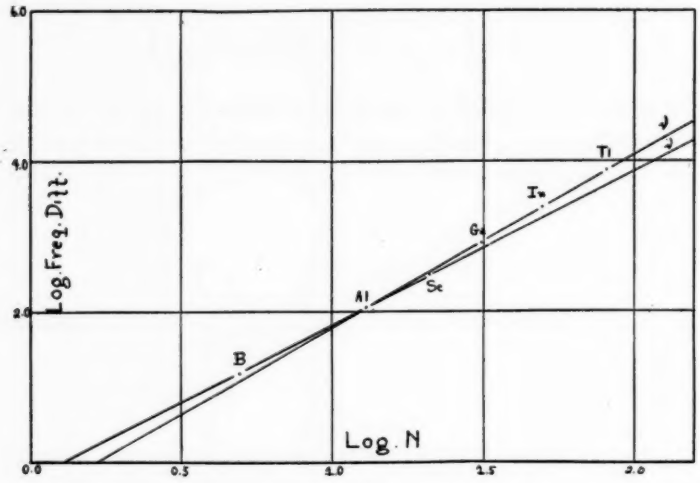

Fig. 6.

TABLE IV.

Element.	*N.*	ν Obs.	ν Calc.	ν Calc. − ν Obs.
Al.....	13	112.07	110.9	− 1.2
Ga.....	31	823.6	829.5	+ 5.9
In.....	49	2212.63	2397.1	+184.5
Tl.....	81	7792.45	7753.5	− 39.0
B.....	5	15.4	12.09	− 3.4

$A = 2.318$
$B = 1.706 = 7 \times .246$

It is seen that the value of the doublet separation in boron lies above the line connecting the points determined by the other elements which are alternate members in the family. If another line should determine the frequency differences for the other elements *B* should lie on it, and it should intersect the known line in the neighborhood of the point determined by Al. Hicks[1] has found a doublet difference for scandium of 320. Combining this value with that known for boron we find that $A = 2.166$, and $B = 1.433 = 6 \times .239$.

DISCUSSION.

The results stated show that the logarithmic method of obtaining the relation between atomic number and frequency differences in spectral

[1] Hicks, Philosophical Transactions, A, CCXIII., p. 408.

series give comparatively good agreement between the observed and calculated values for the constant frequency differences for elements of low atomic number, although the agreement is not within the limit of probable error of the mean of the observed differences, the probable error of the observed value being usually not more than 0.5 cm^{-1}. For elements of high atomic weight the observed values are greater than the calculated, as should be expected if the mass of the electron varies with its velocity. The logarithmic line should, therefore, curve upwards for elements of high atomic weight. Attention is also called to the fact that the calculated values are all too high for the elements which just precede the rare earths in the chemical table.

The importance of the logarithmic line does not lie so much in an attempt to obtain good agreement between observed and calculated values as in the connections which are brought out between different types of series in the same and different chemical families. The equations derived show that the values of B are successive integral multiples of the same constant for the ν, $\nu_1 + \nu_2$, and ν_1 lines in an element. This seems to mean that the frequency differences between the longer wave-length line in triplets and each of the other two are more important than the differences between adjacent lines. The equations give the same value for A[1] for all separations in the same system, and the constants B seem to be integral multiples of the same constant, 0.080, in all systems. The variation of the value of A seems to indicate that spectral series are of several types, just as there are several types of X-ray spectra. In general, the types vary with the valency of the element, but it is possible for the same type to occur in elements with different valencies as is done in groups I. and VI.

The form of the equation derived does not seem to be predicted from the equation for the frequency of lines as developed by Sommerfeld[2] for X-rays, from which we should expect an equation of the type of Bell's to be approximately true. Sommerfeld's equation, moreover, indicates that the convergence frequency of a series should be given by

$$n_0 = \left(\frac{N-k}{p}\right)^2\left[1 + \frac{a}{4}\left(\frac{N-k}{p}\right)^2 + \frac{a}{8}\left(\frac{N-k}{p}\right)^4 \cdots,\right]$$

where a, k and p are constants, a being a small quantity. Therefore, the convergence frequencies of series of the same type should be approxi-

[1] An inspection of the values for A shows common differences of approximately 0.15, the value 2.60 being the only absent member in such an arithmetic series. It is a curious coincidence that the frequency differences between the α and β lines in the K system of X-ray series may be predicted by the equation $\nu = (N/.065)^{2.38}$.

[2] Sommerfeld, Annalen der Physik, LI., 1916.

mately proportional to $(N - N_0)$.[2] That this is not the case is seen from an inspection of Fig. 7, where the convergence frequencies of the series with constant frequency differences have been plotted. The values used were obtained from Dunz, and may also be found in Kayser's Handbuch der Spectroscopie, Vol. II. The graph shows that an approximate linear relation exists between the convergence frequencies and

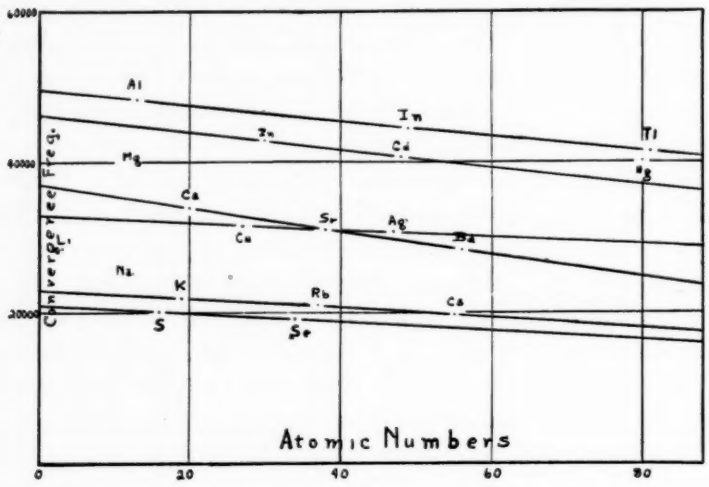

Fig. 7.

atomic numbers of K, Rb and Cs; Ca, Sr and Ba; and Al, In and Tl, which elements I have shown to be related in spectral type. Moreover, a line through the points for S and Se is approximately parallel to that through K, Rb and Cs, a fact which is in support of the hypothesis that the series in these elements is predicted by the same equation.

It would seem that an adequate atomic theory should explain the relation just stated between atomic number and convergence frequency, and the physical reason for the approximate relation

$$\nu = \left(\frac{N}{mnk}\right)^A,$$

where ν represents the frequency difference, N the atomic number, A is a constant, n an integer, both of which vary with the system, m successive integers for the ν, $\nu_1 + \nu_2$, and ν_1 members of the system, and k a constant for all the systems considered.

SMITH COLLEGE,
NORTHAMPTON, MASS.,
February, 1919.

ON THE CHARACTERISTICS OF ELECTRICALLY OPERATED TUNING FORKS.

BY H. M. DADOURIAN.

SYNOPSIS.—A series of experiments was performed to determine the conditions affecting the period of an electrically operated tuning fork with the following results: (1) The more massive the base of the fork and the table upon which it is placed the smaller is the period. This effect, however, is not greater than one part in 10,000. (2) A change in the constants of the electrical circuit containing the electromagnet affects the period. The effect is less than one part in 10,000 for moderate changes necessary for keeping the amplitude of vibration constant. (3) The period increases linearly with the increase in the length of the gaps between the contact springs and contact points. For the forks used this increase was about one part in 500 for a change of 0.1 mm. in the length of the gaps. (4) For a given fork there is an amplitude at which the period has a stationary value. This may be a maximum or a minimum depending upon the arrangement of the mounting of the contact springs. At small amplitudes the change in the period due to a variation in the amplitude may be considerable. (5) The temperature effect increases from 1.04×10^{-4} at $-25°$ C. to 1.43×10^{-4} at 56° C. The values corresponding to temperatures above 0° C. are from 20 to 40 per cent. greater than those obtained by other observers. There are no other published data giving the temperature effect below 0° C. (6) By keeping the temperature, the length of the gap and the amplitude constant, a well-made fork can be relied upon to give a constancy of rate accurate to one part in 50,000. (7) The theoretical expression for the period of vibration of a bar holds good for a tuning fork. (8) The velocity of sound in the steel of which the forks used were made is 5.49×10^5 cm. per sec. (9) The coefficient of modulus of elasticity of the steel is 19.10×10^{11}. (10) The temperature coefficient of the modulus of elasticity increases from -2.2×10^{-4} at $-25°$ C. to -2.96×10^{-4} at 56° C. These values were computed from the relation $\epsilon = -(2\theta + \alpha)$, where ϵ is the temperature coefficient of modulus of elasticity, θ the temperature effect upon the period of the fork, and α the coefficient of linear expansion of steel.

I. INTRODUCTION.

THE determination of the frequency of tuning forks and the study of the causes affecting the frequency have been the subjects of investigation by a large number of physicists during the last hundred years or more. Consequently the author would not have thought of carrying out the researches described in the following pages had not circumstances led him to them. While working on problems of sound ranging with the Engineer Detachment of the United States Army in Princeton, it became part of the author's work to adjust and to determine the periods of vibration of a number of tuning forks. As these forks were slightly different in shape and in details of mounting from those used

by previous investigators it was found desirable to know the extent to which the results obtained by them held good for these forks. A brief investigation was therefore planned with this end in view. But as the work progressed, interesting and important results were obtained which led the author to widen the scope of inquiry until the problem had been carefully studied in all its phases.

II. DESCRIPTION OF THE FORKS.

Most of the experiments described in the following pages were carried out with forks made by the Western Electric Company, of the type shown in Fig. 1. The fork proper is milled out of a solid piece of soft machine steel and is electro-galvanized to prevent rusting. The prongs of the fork are about 39.5 cm. long, 0.95 cm. thick, 1.90 cm. deep, and 2.90 cm. apart. The outer curves at the shoulders as well as the inner curve are circular. Consequently the prongs are thinner at the shoulders than the prongs of standard Koenig forks of the same general dimensions, and therefore vibrate about their fixed ends as axes more like rigid bars than do the prongs of the Koenig type of fork.

The fork is rigidly attached to the back of a brass casting which has the form of a rectangular trough. The electromagnet is provided with movable pole-pieces placed on the outside of the prongs. This feature had been introduced by the Western Electric Company to satisfy the special conditions for which the fork was originally designed and is not at all necessary for its general serviceability. In fact the common type of electromagnet with pole-pieces between the prongs is preferable for a fork for which constancy of frequency is the principal desideratum.

A steel contact spring, 0.28 mm. thick and 3.92 mm. wide, is attached to each of the prongs by means of a steel clamp screwed to the prong at a point about midway between its ends. The contact spring is reënforced with two shorter springs placed one on each side and clamped together. When the fork is adjusted the free end of each contact spring comes midway between two platinum contact points soldered to the ends of two brass screws. The latter are set in brass bars provided with set screws for the purpose of making the contact screws fast after adjustment. These bars are screwed to a piece of micanite which forms the top piece of the bridge over the prongs. In order to secure good electrical contact a circular piece of platinum foil is soldered to each side of the free end of each contact spring.

The scheme of electrical connections is shown in Fig. 2, where the arrowheads marked A, B, C and D indicate the four contact points at the ends of the horizontal brass screws shown in Fig. 1. The condensers

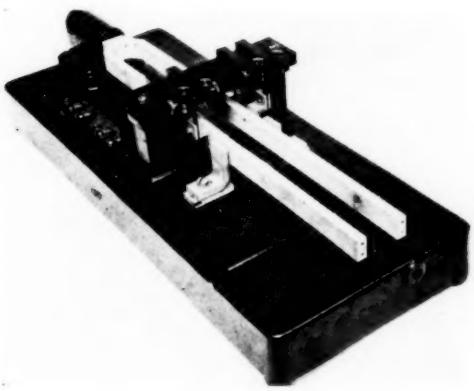

Fig. 1.

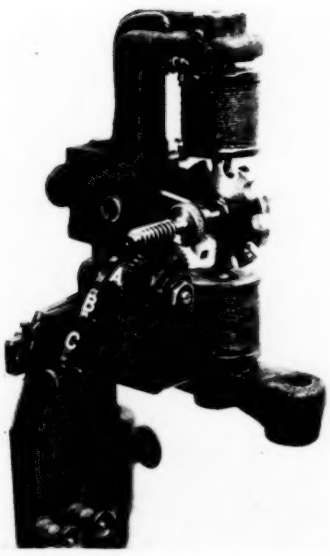

Fig. 4.

H. M. DADOURIAN.

marked *c* have each a capacity of 0.5 M.F., the resistance coils marked *r* have each a resistance of 150 ohms, and the field coil, *R*, of the electromagnet has a resistance of 225 ohms and about 6,300 turns of wire. The condensers and the resistance coils are attached to the under side of the brass base. The contact points *C* and *D* do not form parts of the electrical circuits, but they are necessary for the symmetry of the mechanical action of the contact points upon the contact springs. The contact point *D* is provided with the necessary connections, so that it can be made use of electrically in case it is desired to energize the electromagnet of the phonic wheel every half period instead of every full period,

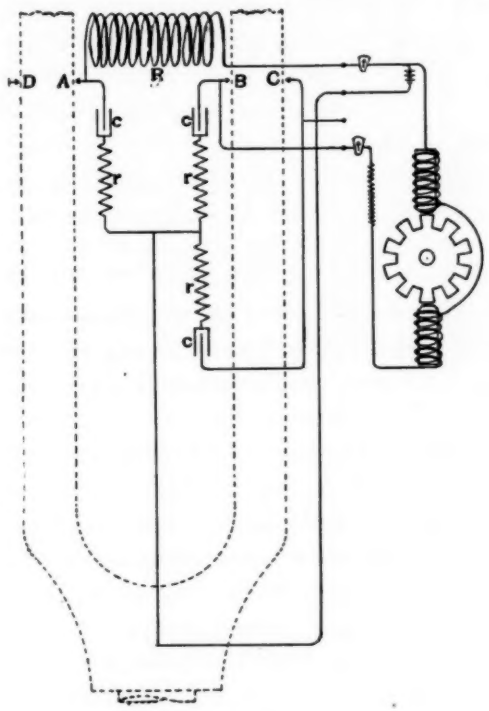

Fig. 2.

for instance. It may be stated here parenthetically that the wheel runs with greater smoothness between two than between four pole-pieces as the fork functions under normal running conditions remarkably free of sparking at the contact points, so that the pieces of platinum foil soldered at the ends of the contact springs last indefinitely.

In addition to the W. E. (Western Electric) forks three others were used. One of these was a Leeds and Northrup fork kindly loaned by the Company. Another was a fork made by Pirard and Coeurdevache of

Paris. The third was an old 50 V. D. Koenig fork mounted upon the base of one of the W.E. forks. In order to adapt the Koenig fork to the W.E. base, contact springs were clamped to the sides of the prongs at points about one-fourth of the length from the free ends. The way in which this was done is indicated in Fig. 3, where *A* is a piece of steel channeled to a depth slightly less than the total thickness of the three springs between it and the prong. This piece was attached to the prong by means of two screws which pass through holes made in the springs. The arrangement is an improvement over that of the original W.E. forks, first because it is simpler and second because it does not unnecessarily modify the uniformity of the effective thickness of the prong in the neighborhood of the clamp, as the spring in contact with the prong has only one-third the width of the clamp in contact with the prong in the W.E. fork.

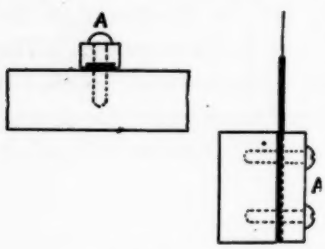

Fig. 3.

III. Method of Determination of the Period.

The period of vibration of the fork was determined by a method devised by Captain H. B. Williams. Chronographic records of every fiftieth complete vibration were compared with the records of the mean-time clock of the Princeton University Observatory. In order to record the vibration the phonic wheel and contact making device shown in Fig. 4 were used as intermediary between the fork and the chronograph. When the fork is set in vibration the circuit, of which the field coils of the phonic wheel form a part, is made and broken at the contact point *A*, Fig. 2, thus periodically exciting the electromagnet of the wheel. If the armature of the wheel is given a motion of rotation so that one of its teeth comes nearly in front of each of the pole-pieces of the magnet it falls in step with the magnetization of the electromagnet and rotates synchronously with the vibration of the fork. The rotation of the armature causes the toothed wheel *A*, Fig. 4, to rotate and to push against the rod *B* every time one of its teeth passes by the end of the latter. The rod *B* then comes into contact with the rod *C*, thus closing the circuit which operates the pen of the chronograph. The gearing intervening between the phonic wheel and the contact maker is such that this occurs once in every fifty complete vibrations of the fork. The short flat springs at the lower ends of the rods *B* and *C* hold them in position and connect them to the binding post at the lower left hand corner of Fig. 4 to which are attached the leads of the chronographic

circuit. The time of contact may be made as short as desired by adjusting the position of the contact maker relative to the wheel *A*, and of the rod *C* relative to the rod *B*. The clock records were obtained by the intermediary of a quick contact making device, attached to the scope wheel of the observatory clock, of which the contact maker shown in Fig. 4 is a simplified copy.

The phonic wheel was invented by La Cour and Rayleigh, independently. They used it, however, to compare the frequencies of two forks by the stroposcopic method and not to obtain chronographic records of a fork. The method described in the preceding paragraph which may, properly, be called the *chronographic method*, is more convenient and is capable of yielding a greater accuracy than any other method hitherto used for determining the period of a tuning fork, as will be observed from the following statement.

First, in the chronographic method a record of two hours can be obtained without any more care on the part of the experimenter than that of winding up the clock-work of the chronograph. The record obtained can be read with great precision, and being permanent can be read at one's convenience and kept for future reference. The clock does not have to be adapted to the fork nor the fork to the clock; consequently the frequency of any fork can be obtained by comparing its record with that of the clock, the rate of which is practically constant and known very accurately. The rate of the mean time clock used in these experiments was known to one part in 200,000.

Second, in this method the recording arrangement does not affect the motion of the fork as in the case of the vibrographic method in which the variable pressure of the drum against the recording style must have an appreciable effect upon the period of the fork. In this connection it may be stated that an experiment was performed in which the period of W.E. fork No. 496 was observed while the mean current through the field coils of the phonic wheel was changed from 60 to 180 milliamperes, but no appreciable change in the period was observed.

Third, the method gives a direct comparison of the fork with a primary standard like a clock, and not with a secondary standard in the form of another fork.

The precision of the chronographic method depends upon (*a*) the accuracy with which the rate of the clock is known, (*b*) the accuracy of the positions of the fork signals relative to the positions of the clock signals on the chronographic record, (*c*) the length of the record, and (*d*) the precision with which it is read. The error due to the rate of the clock may be made negligible by using a clock the rate of which is accurately

determined. The error due to the irregularities of the positions of the signals need not be more than .01 sec. in a well-constructed instrument. The chronographic record can be read with great accuracy by means of a differential scale often used by astronomers. So that even if an error of .05 sec. is made, due to the imperfections of the recording apparatus, the effect of this comparatively large error can be made negligible by taking a fairly long record. If the record is an hour long, for instance, an error of .05 sec. due to the end signals will introduce in the determination an error of one part in 72,000 only.

IV. EFFECT OF BASE.

It follows from theoretical considerations that the base upon which the fork is mounted should have no mass at all or it should have an infinite mass in order that it absorb no energy from the fork. It is to be expected therefore that the base of a fork will have some effect upon the period. In order to study this effect the following experiments were performed.

The W.E. fork No. 496 was placed upon a brick pier with a marble top and its period determined. A lead weight of 10 kg. was then placed upon the standard by means of which the fork proper is attached to its base and the period was again determined. The result of increasing the mass of the base by this means was to decrease the period by one part in 30,000.

A similar experiment was made with the Pirard and Coeurdevache fork and a decrease of one part in 1,000 observed. The reason for the comparatively large change in the period of this fork can be accounted for by the fact that the P. & C. fork weighs about 4 kg. while the W.E. forks weigh about 12 kg.

Next the effect of the table upon which the W.E. fork was placed was determined by observing its period while it was (*a*) upon the pier, (*b*) upon a wooden table and (*c*) upon a shaky stool. The result was a progressive increase in the period, the period on the stool being one part in 10,000 greater than on the pier.

The relatively large weight of the base and mounting of the W.E. forks is therefore a desirable feature, which makes the effect on the period of the mass of the table upon which it is placed relatively small.

V. EFFECT OF CHANGES IN THE CONSTANT OF THE ELECTRICAL CIRCUIT.

In Fig. 5 let oo' indicate the position of rest of the contact spring which is in series with the field coil of the electromagnet, bb' and cc' indicate the positions of extreme displacement, and aa' its position at the

instant it comes into contact with A, Fig. 2, and closes the circuit of the electromagnet. On account of the self induction of the circuit the driving current does not attain its maximum value instantaneously but increases according to the well-known exponential law during the excursion of the spring from aa' to bb' and back to aa'. At aa' the spring leaves the contact point thus opening the circuit and permitting the current to die down. The values of the current at different parts of a complete vibration are roughly indicated by the curve $ab'a'ca$. The motion of the prongs is opposed by the magnetic field, while the spring moves from aa' to bb', is helped while moving from bb' to cc' and is opposed again while moving from cc' to aa'. Thus the motion of the prongs is opposed during the time the prongs come together and is helped the rest of the time. Therefore a periodic but non-harmonic force is impressed upon the prongs in addition to the forces of restitution and of damping. When a steady state of vibration is reached the energy supplied per cycle by this force equals the energy dissipated by the damping forces. This energy is a function of the area enclosed by the broken curve $ab'a'ca$. The area as well as the position of its center can be altered while the maximum value of the current is kept constant by changing the constants of the exponential curves and the position of the line aa'. In other words the energy applied per cycle and the effective phase of its application may be altered by changing the time constant of the circuit and the length of the gap between the spring and the contact point.

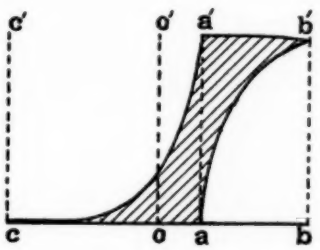

Fig. 5.

It will be seen in Part VII. that for constancy of frequency it is necessary to keep the amplitude constant. But to do this it may be necessary to regulate the driving current and hence it is of importance to know to what extent, if at all, a change in the time constant due to a change in the resistance of the circuit affects the period while the amplitude is kept constant. This point was investigated with the W.E. fork No. 488 in two experiments. In one of these the effect of an additional non-inductive resistance was observed, and in the other the effect of adding a self induction to the circuit was determined, the amplitude being kept constant in both cases. The results of the first experiment are shown by the curves of Fig. 6, where the abscissas denote the external non-inductive resistance added to the circuit of the electromagnet, and the ordinates denote the percentage increase in the period of the fork in ten-thousandths parts of the period corresponding to zero external resistance.

Curve I. was obtained with the length of the gaps between the contact springs and the contact points equal to .05 mm., while curve *II.* was obtained with the length equal to 0.3 mm. It will be observed that the effect is greater for the longer gap. But the effect is negligible for both, so long as the change in the resistance is small. If a change of 100 ohms is made in the resistance of the circuit to keep the amplitude constant,

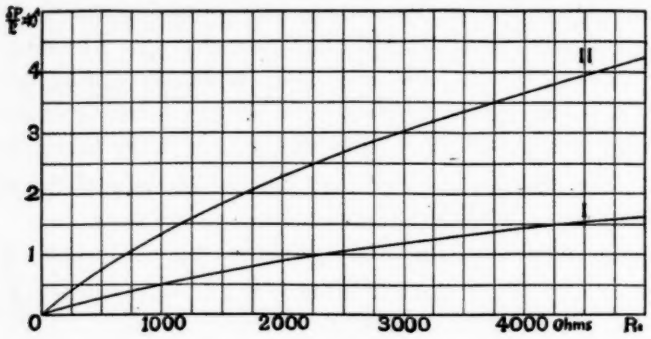

Fig. 6.

the change in the period is under one part in 100,000 for curve I. and under two parts for curve *II.*

The effect of an increase in the self induction of the circuit was next observed by placing alternately an inductive resistance and a non-inductive resistance of equal value in series with the coil of the electromagnet and the change in the period was found to be less than one part in 10,000.

VI. Effect of the Length of the Gap.

It is evident from Fig. 5 that a change in the position of the line *aa'* would result in a change in the area of the cycle *ab'a'ca* and the position of the center of this area. Consequently changing the gap between the contact spring and the contact point introduces a change in the amount of energy applied to the fork per period and in the phase of application of this energy. Furthermore the circumstances of the mechanical action of the contact points upon the springs, and through them upon the prongs, is changed when the gaps are changed. Therefore an alteration in the length of the gaps is bound to affect the period of vibration of the fork.

This effect was studied by determining the period of vibration for gaps of different lengths. The results of an experiment with the W.E. fork No. 488 are shown by curve *I* of Fig. 7, where the abscissas denote the lengths of the gaps between the springs and the contact points in fractions of one millimeter, while the ordinates denote percentage increases in the period in ten-thousandths of the period corresponding to zero gap.

All four of the gaps were made of the same length, changing them from .04 mm. to .25 mm. in ten steps. It will be observed that the effect is very nearly linear and that it is comparatively large, being one fifth of one per cent. per one tenth of a millimeter change in the length of the gaps.

Curve *II* was obtained with the Koenig fork. In spite of the fact that the springs were less stiff than those of fork No. 488 the gap-effect of the Koenig fork is greater than that of No. 488. This can be accounted for

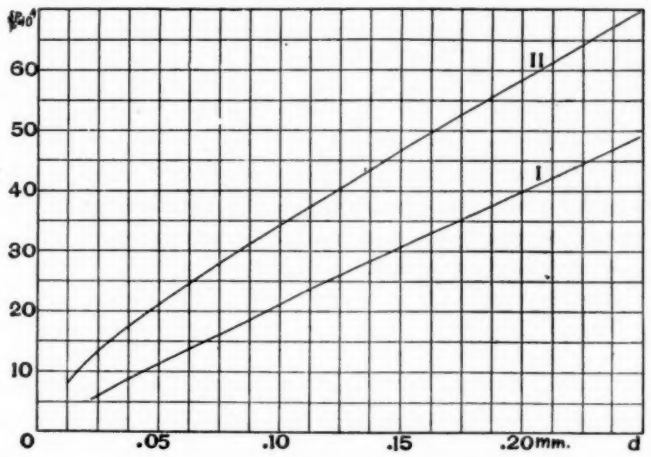

Fig. 7.

by the fact that the springs were nearer the free ends of the prongs in the case of the Koenig fork and consequently the moment of the forces acting upon the springs was greater in proportion, and that the forks were relatively thinner and consequently their motion was more easily affected by this moment.

These results show that the gap-effect is considerable and that the gaps must be kept constant in length if constancy of frequency is desired. This fact does not seem to have been recognized by students and makers of tuning forks, as is evident from the form of contact springs of standard types of forks. Most of these forks have twisted platinum wires for contact springs which change their shape under the action of the contact points, making the length of the gaps variable. The springs of the W.E. forks can be relied upon to keep their shape and position so that the length of the gaps do not vary more than .01 mm.

It was found that the positions of the springs relative to the contact points were slightly changed when the position of the fork was changed. This was due to a redistribution of the weight of the fork among the four

rubber feet of the base and the consequent strain in the frame of the base. In order to avoid possible errors from this source, the gaps were examined whenever the forks had to be moved and one of the feet raised by placing a few thicknesses of paper, thereby bringing the springs to positions midway between the contact points. This precaution can be made unnecessary by making the frame of the base more rigid and providing it with three instead of four feet.

The effect upon the period of fork No. 488 of eliminating the outer contact points was determined by observing the period alternately with the outer contact points at 0.1 mm. from the springs and at distances beyond the reach of the springs. The average results of four separate determinations was to change the time of 50 periods from 1.00096 sec. with the outer contact points at 0.1 mm. to 1.00369 sec. with the outer contact points beyond the reach of the springs, the inner contact points being kept at 0.1 mm. from the springs. In other words the mechanical action of the outer contact points upon the springs decreases the period by a fraction of about 27 parts in 10,000.

VII. Effects of Changes in Amplitude.

Mercadier[1] and Ettinghausen[2] have observed that the frequency of a fork increases with decreasing amplitude and approaches assymptotically the frequency corresponding to zero amplitude. Poske[3] and Heerwagen[4] on the other hand have found that the frequency increases linearly with decreasing amplitude. Heerwagen has expressed his results by the equation

$$n = n_0 - p\alpha$$

where n and n_0 denote the frequency, α the amplitude, and p a constant. Hartmann-Kempf[5] has observed, however, that the frequency increases more rapidly than Heerwagen's linear equation would imply and has expressed his results by the empirical relation

$$n = n_0 - (p + \Delta\alpha)\alpha.$$

The differences in the conclusions attained by these investigators can be accounted for in the light of the results obtained from the following experiments upon the effect of changes of amplitude upon the period. Throughout these experiments the temperature and the spark gaps were kept constant. The amplitude was measured by means of a traveling

[1] Mercadier, C. R., 83, p. 800, 1876; Journ. de Phys., 5, p. 201, 1876.
[2] A. Ettinghausen, Pogg. Ann., 156, p. 337, 1875.
[3] H. Poske, Pogg. Ann., 152, p. 448, 1874.
[4] F. Heerwagen, Diss. Dorpat, 1890.
[5] R. Hartmann-Kempf, Ann. d. Phys., 13, p. 124, 1904.

microscope provided with a vernier to read twentieths of one millimeter. The microscope was focused upon a bright spot at the end of one of the prongs and the double amplitude measured; the double amplitude of the other prong was then measured and one half of the average of the two observations taken as the amplitude of the fork.

Curves *I* and *II* in Fig. 8 show the results obtained with the W.E.

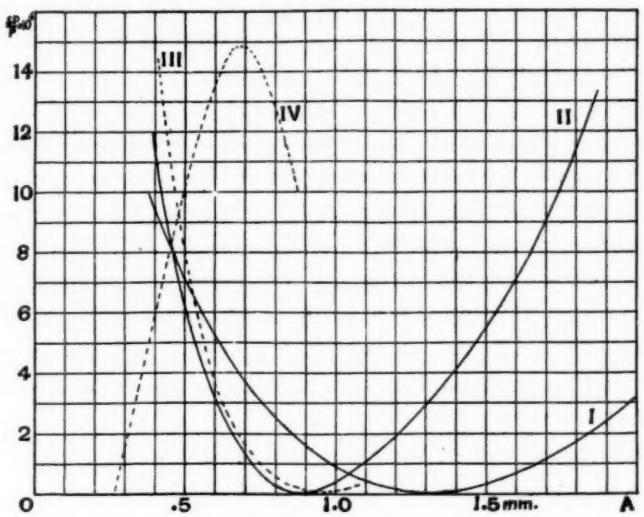

Fig. 8.

fork No. 496. The abscissas denote single amplitudes in millimeters and the ordinates denote percentage increases in the period in ten-thousandths of the minimum period observed. The changes of amplitude of curve *I* were made by increasing the current in the field coils of the electromagnet while the pole-pieces were kept fixed. On the other hand, the changes in the amplitude of curve *II* were obtained by moving the pole-pieces relative to the prongs while the current was kept constant. The curves represent the averages of two sets of curves, one obtained by increasing the amplitude and the other by decreasing it. The two component curves did not quite coincide; each formed, however, a very smooth curve representing the experimental data.

These curves bring out the interesting fact that there is an amplitude for which the period has a minimum value. In other words there is an amplitude in the neighborhood of which the period has a stationary value and consequently is not affected by small changes of amplitude. The value of this amplitude is different for the two curves because of the difference in the manner in which the changes were brought about. We shall see later that the amplitude corresponding to the stationary

value of the period depends also upon the stiffness of the contact springs and upon the length of the gaps.

Curve *III* was obtained with the Leeds & Northrup fork. It will be observed that it has the general shape of curves *I* and *II*. This was to be expected because the Leeds & Northrup contact arrangements are somewhat similar to those of the W.E. forks. Curve *III* and curve *IV* could not be extended further to the right because the amplitude could not be increased beyond certain limits on account of the proximity of the prongs to the pole-pieces of the electromagnet.

Curve *IV* was obtained with a Pirard & Coeurdevache fork. In this case the period has a maximum instead of a minimum value because in the P. & C. fork the contact springs as well as the contact points are attached to the base and consequently the prongs are not in contact with the springs during a fraction of the period which forms a greater and greater portion of the period as the amplitude is increased. This explanation is sustained by the experiment described in the last paragraph of Part VI. where it was shown that relieving the prongs from the mechanical action of the outer contact points resulted in a considerable increase in the period.

Amplitude-period curves were also obtained for the Koenig fork and

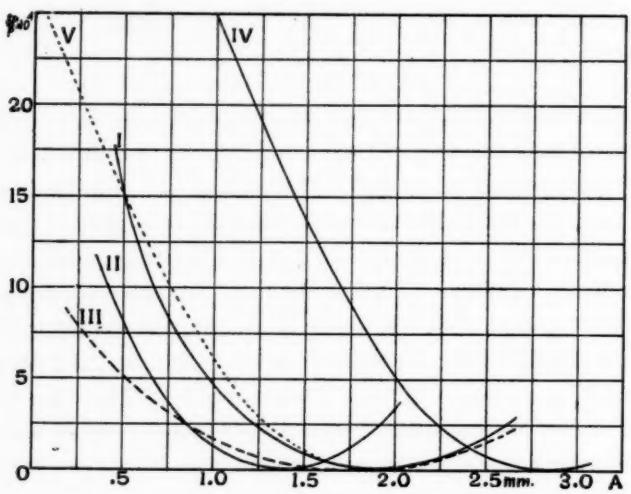

Fig. 9.

for the W.E. fork No. 488. Curve *III* of Fig. 9 was obtained with the Koenig fork, the changes in the amplitude being obtained by changing the driving current, while curves *I* and *II* were obtained with the W.E. fork No. 488. In the experiments corresponding to curve *I* the pole-pieces of the magnet were moved; in the experiment corresponding to

curve *II* the driving current was changed. It will be observed that as in the case of fork No. 496 the amplitude corresponding to the minimum period is smaller for curve *I*.

Curve *IV* was obtained with the 488 fork under the same conditions as curve *I* except that the gaps were changed from .05 mm. in the case of curve *I*, to 0.30 mm. in the case of curve *IV*. In order to compare these two curves, curve *V* similar to curve *IV* was drawn so that its minimum point coincides with that of curve *I*. It will be observed that the rate of decrease of the period is greater for *I* than for *V*. This can be accounted for on the ground that for a given magnitude of the mechanical action of the contact points upon the springs, the energy of the prongs was greater in the experiments corresponding to curve *V*. This explanation is in accord with the fact that the curves are steeper to the left of the minimum point, where the amplitude is smaller and consequently the energy of the prongs is smaller.

From the foregoing considerations it will be expected that for a given length of gap and at a given amplitude less than the amplitude which corresponds to the stationary value of the period, the rate of decrease

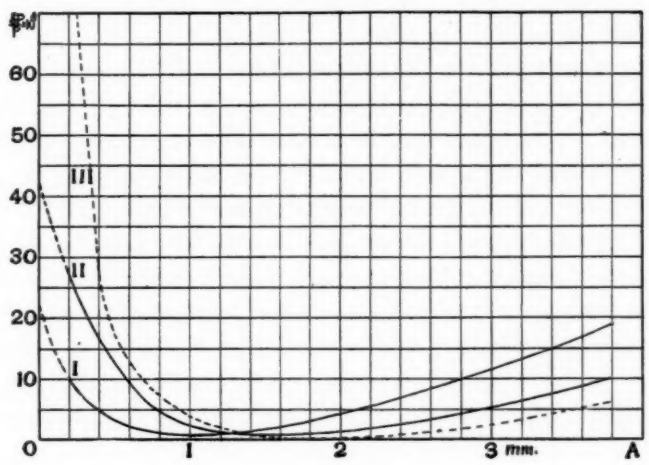

Fig. 10.

of the period will be smaller the smaller the stiffness of the springs. Certain experiments, the results of which are indicated by the curves of Fig. 10, sustain this conclusion. All three of these curves were obtained with fork No. 488 with gaps equal to .05 mm., the amplitude being altered by changing the driving current. In the experiment represented by curve *I* the fork had the same contact springs as in the experiment of curve *I* of Fig. 9, namely, springs with cross-sections of .41 mm. × 4.64 mm.

In the experiments represented by curves *II* and *III* the fork had springs with cross sections 0.28 mm. × 3.92 mm., and .48 mm. × 7.86 mm., respectively. A glance at these curves shows that the stiffer the springs the steeper are the curves on both sides of the minimum point, and the greater is the amplitude corresponding to the minimum period.

The results of other experimenters can be made to agree among themselves and with the results obtained by the author if it is supposed that the former have to do with that part of the period-amplitude curve which lies to the right of the minimum point and that the region investigated by Mercadier and Ettinghauser comes nearer the point of minimum period than the region studied by Poske, Heerwagen and Hartmann-Kempf.

The more important results of the experiments described in Part VIII. may be summarized in the following terms.

First, the period-amplitude curve passes through a stationary value and consequently there is an amplitude at which the fork can be operated with maximum constancy of period.

Second, the amplitude which corresponds to the stationary value of the period depends upon the stiffness of the contact springs and the length of the gaps.

From the results of the experiments described in Parts V. and VI. certain inferences may be drawn with regard to the best position for the contact springs. For a given contact pressure the action of the contact points upon the springs, and through them upon the prongs, is greater the nearer the springs are placed to the free ends of the prongs. Furthermore, for a given change in the amplitude the change in the contact pressure is greater the nearer the springs are placed to the free ends. On the other hand there is a limit to the extent to which the position of the springs can be approached to the shoulders of the fork. Hence there must be a position which is more favorable than any other. The determination of this position did not form a part of the investigations described here, but considerations based upon the mechanical action of the contact points upon the prongs, the position of center of percussion of the prongs, and the nodal points of the first harmonic of the vibration have led the author to the conclusion that the most favorable position for the contact springs must lie between the middle of the prong and one third of the distance from the free ends.

VIII. Temperature Effect.

A score or more physicists have determined the effect of temperature upon the frequency of tuning forks and have obtained concordant results.

These men, however, do not appear to have appreciated the importance of controlling certain factors which we have found to affect the frequency. It was deemed worth while, therefore, to redetermine the temperature effect under the favorable conditions which could be secured in the light of the experiments described in the preceding pages. Another reason which induced the author to carry his investigations into this phase of the tuning fork problem was the fact that he had at his disposal facilities to extend the investigation on the temperature effect to temperatures below zero degree centigrade, to which region the older investigators had not carried their work.

The work was carried on in the constant temperature rooms of the Palmer Physical Laboratory. The larger of the two rooms was provided with a thermostat which responded readily to changes of temperature as small as 0°.1. The smaller room had no temperature regulating device but its temperature could be lowered still further. Two separate determinations were made. The first, made in the larger room, covered the range of temperatures between − 3°.6 C. and 56°.8 C. The second, made in the smaller room covered the range of temperatures between − 25°.8 C. and 21°.2 C.

The W.E. fork No. 488 and the Koenig fork were placed side by side on a table in the middle of the larger room and a box with open ends was built over them. A microscope with a scale in the ocular was focused upon a bright spot at the end of one of the prongs of each fork, in order to observe and adjust the amplitude of vibration. Two thermometers made by R. Fuess with ranges of − 30° C. to 100° C. and scales divided into tenths of one degree were suspended so that the bulb of one was placed between the prongs and near the stem of one of the forks. A Callander recorder was set up to observe the temperature without going into the constant temperature room in use, but it was found to be not quite sensitive enough to give the temperature to the desired degree of precision; therefore it was used only to keep a rough record of the changes. The following general method of procedure was used during the first experiment: About one half hour after the temperature of the room had reached a desired value the room was entered and the gaps of the forks were examined to see if there had been any changes in the lengths of the gaps from the value .05 mm. to which they had been adjusted. Each fork was then set into vibration and the amplitude adjusted, if necessary; fork No. 488 was left vibrating and the open ends of the box were covered with pieces of woolen cloth. After about ten minutes the room was entered again, the thermometers read (this could be done without opening the box), and the chronograph started. Twenty

minutes later the room was entered again, the thermometers were read, the Koenig fork was started and its record also taken for twenty minutes, after which the thermometers were read again. In this manner a large number of records were obtained which covered the range of temperatures between − 3°.6 C. and 56°.8 C. and extended over several days.

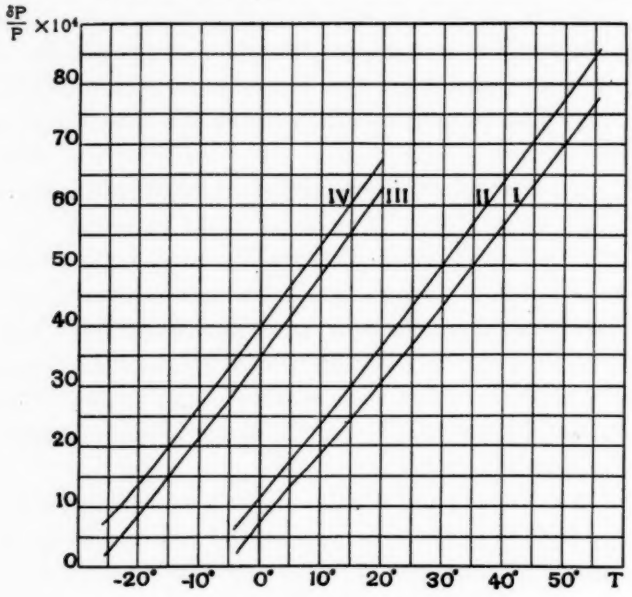

Fig. 11.

The results obtained with fork No. 488 were plotted on a large scale upon a millimeter cross-section paper with the temperatures as abscissas and the corresponding values of 50 complete periods as ordinates and a smooth curve was obtained with a continuously increasing slope. From this curve *II* of Fig. 11 was drawn, where the ordinates give the percentage increases in the period in ten-thousandths of the period at 0° C.

The period-temperature curve of the Koenig fork had an inflection point at about 11° and another at about 35°. There is no doubt that this behavior of the Koenig fork was due to slight variations in the spark gaps observed during inspections of the gaps made before taking records. The variation in the gaps must have been due to the expansion and contraction of the vulcanite piece which carried the contact points. In the regular W.E. forks this piece was of micanite which has a much smaller coefficient of expansion. Curve *I* which represents the results obtained by the Koenig fork is therefore of interest because it shows the importance of having spark gaps of constant length as well as because it supports the general conclusions derived from the other three curves of Fig. 11.

In the second experiment the Koenig fork was replaced by the W.E. fork No. 313 and the apparatus was set up in the smaller room. This room did not have a thermostat and consequently its temperature could not be kept constant; therefore the following method of procedure was adopted. The room was cooled several degrees below the temperature in the neighborhood of which it was desired to take a record; then the refrigerating machine was stopped and the temperature was allowed to rise for several hours and then records of the two forks were taken in the same manner as in the first experiment. This was repeated until ten pairs of records were taken while the temperature was lowered in the manner just described from 21°.2 C. to − 27°.C. The temperature of the room was then allowed to rise from − 27° to the normal room temperature and 15 more pairs of records were taken. The experiment took eight days and the rate of change of temperature was so slow during the intervals when records were taken that the temperature could be considered as constant. The results of this experiment are indicated by

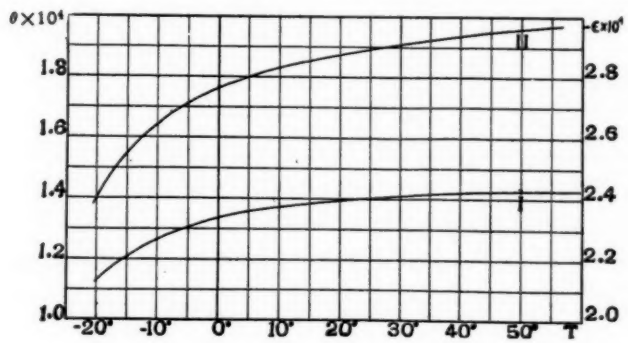

Fig. 12.

curves *III* and *IV* of Fig. 11, curve *III* corresponding to No. 488 and curve *IV* to No. 313.

The results indicated by the curves *II*, *III* and *IV* were plotted accurately on a large scale and the different rates of increase in the period at different temperatures were determined for each curve. The average values for the three curves are given in Table I., where the numbers in the first column represent the temperatures and those in the second column the corresponding values of the temperature coefficient θ defined by

$$\theta = \frac{1}{P_0}\frac{\partial P}{\partial t},$$

or

$$P = P_0(1 + \theta t).$$

TABLE I.

t.	θ.	$-\epsilon$.	t.	θ.	$-\epsilon$.
− 20°	1.14×10^{-4}	2.39×10^{-4}	20°	1.38×10^{-4}	2.87×10^{-4}
− 10°	1.27	2.65	30°	1.40	2.91
0°	1.33	2.77	40	1.42	2.95
10°	1.36	2.83	50°	1.43	2.97
			− 20 to 50	1.34	2.79

These results are represented graphically by curve *I* of Fig. 12. The values of θ given in Table I. are from 10 to 40 per cent. higher than the average value of the results obtained by former observers as will be seen from Table II.

TABLE II.

Observer.	Range of Temp.	Temp. Coef.	Observer.	Range of Temp.	Temp. Coef.
Mercadier[1]	3°–26°	0.96×10^{-4}	Michelson[5]	12°–24°	1.00×10^{-4}
Kayser[2]	0°–26°	0.98	Lang[6]	14°–19°	1.11
Koenig[3]	3°–26°	1.11	Pierpaoli[7]	0°–30°	1.05
Koenig[3]	26°–56°	1.07	Woodruff[8]	20°–200°	1.08
McLeod & Clarke[4]	15°–26°	1.10	Dadourian	− 26°–57°	1.34

It will be shown in Part XII. that the effect of temperature upon the period of a fork is mainly due to its effect upon the elasticity of the fork and that only about 5 per cent. of the former effect is due to the increase in the dimensions of the fork resulting from a rise of temperature.

IX. CONSTANCY OF PERIOD.

The constancy of the performance of the W.E. fork No. 488 was tested under the following conditions: The pole-pieces of the electromagnet were set at 1.37 mm. from the prongs. The contact points were adjusted so that the length of the gaps was .05 mm. A potential of 24 volts was applied directly to the binding posts on the fork. Under these conditions an amplitude of 1.58 mm. was obtained which corresponds to the stationary period of the fork under the given conditions. The fork was operated continuously from 8.43 a.m. until 12.45 M., and chronographic records were taken. The period was then determined for different parts

[1] Mercadier, Journ de Phys., 5, p. 201, 1876; C. R., 83, p. 822, 1876.
[2] Kayser, Wied. Ann., 8, p. 444, 1879.
[3] Koenig, Wied. Ann., 9, p. 394, 1880.
[4] McLeod & Clarke, Phil. Trans. Roy. Soc., 171, part I., p. 1, 1880.
[5] Michelson, Am. Journ. Sci., 25, p. 61, 1883.
[6] Lang, Wied. Ann., 29, p. 132, 1886.
[7] Pierpaoli, Rend Linc., 4 (1), p. 714, 1888; 5 (2), p. 265, 1889.
[8] Woodruff, PHYS. REV., 16, p. 325, 1903.

of the run from careful measurements of the record, taking intervals of 20 minutes. The results of these determinations are given in Table III. where the numbers in the first column give the temperatures at the middle of the different 20-minute intervals, those in the second column are the corresponding observed values of 50 complete periods, the numbers of the third column are these values corrected to 20°.50 C. and those of the last column are the percentage deviations of the values of the periods thus determined from their mean value.

TABLE III.

Temperature.	50 P.	50 P_c.	$\delta P/P$.
20°.30	1.000885 sec.	1.000913 sec.	-8.4×10^{-6}
20°.34	1.000903	1.000925	3.6
20°.38	1.000910	1.000927	5.6
20°.46	1.000925	1.000931	9.4
20°.50	1.000336	1.000934	13.6
20°.56	1.000934	1.000926	4.6
20°.66	1.000923	1.000901	− 20.4
20°.69	1.000940	1.000913	− 8.4
20°.72	1.000954	1.000923	1.6
		1.0009214	± 8.4

Another set of determinations was made the next day with the spark gaps equal to 0.3 mm. the pole-pieces at 1.0 mm. from the prongs, and an amplitude of 1.75 mm. The fork was operated from 12.55 until 4.19 P.M. and a continuous record taken. The values of 50 periods were then determined as in the preceding experiment and the results given in Table IV. were obtained.

TABLE IV.

Temperature.	50 P.	50 P_c.	$\delta P/P$.
20°.77	1.004153 sec.	1.004134 sec.	-10×10^{-6}
20°.74	1.004168	1.004155	11
20°.72	1.004186	1.004175	31
20°.70	1.004181	1.004170	26
20°.67	1.004152	1.004148	4
20°.65	1.004153	1.004151	7
20°.63	1.004136	1.004137	− 7
20°.62	1.004126	1.004136	− 8
20°.61	1.004115	1.004122	− 22
20°.60	1.004114	1.004121	− 23
		1.0041443	± 14.9

A glance at the last columns of Tables III. and IV. shows the remarkable constancy of performance of the fork. In the first run the maximum

deviation from the mean for a run of four hours is only one part in 50,000 while the average deviation is less than one part in 100,000. In the second run the deviation from the mean is larger. But in this case the deviation is systematic indicating that the conditions affecting the period were not kept as constant as during the first run. The great constancy of performance shown by the fork is all the more remarkable because it is a commercial article in the manufacture of which no great effort had been made to secure such important requirements as a high degree of uniformity of thickness of prongs and symmetry relative to the axis of the fork. This investigation shows conclusively that a proper control of the factors affecting the period is of prime importance.

X. EXPRESSION FOR PERIOD OF VIBRATION.

It has been shown by Mercadier[1] that the expression for the period of transverse vibration of a bar obtained from the theory of elasticity holds good for a tuning fork provided the projection of the median line of the prongs upon the geometric axis of the fork is taken for the length of the prongs and a small correction term is added to this. The expression for the period of vibration of a bar is

$$P = \frac{4\pi\sqrt{3}}{r^2 v}\frac{l^2}{a} \tag{1}$$

where l is the length and a the thickness of the bar, v the velocity of sound in the bar, and r the root of the equation

$$(e^r + e^{-r}) \sin 2r + 2 = 0 \tag{2}$$

and equals 1.87011.[2] For rods of the same material v is constant, therefore we can write

$$P = K\frac{l^2}{a} \tag{3}$$

Mercadier's modified expression for tuning forks is

$$P = K\frac{(l+\lambda)^2}{a} \tag{3'}$$

where λ is a correction term introduced in order to satisfy Mercadier's experimental results and equals $.012l$. Evidently the value of λ will depend upon the shape of the fork near the shoulders of the prongs. Since the W.E. forks had a slightly different shape from those used by Mercadier it was thought desirable to determine the value of λ for these forks. Using Mercadier's experimental value of K, namely, 1/81,827

[1] E. Mercadier, C. R., 79, pp. 1001, 1069, 1874; Journ. de Phys., V., p. 201, 1876.

[2] Poisson, Traité Mecanique, II., p. 390.

sec./cm., the values given in the first column of Table V. were obtained for ten different forks.

TABLE V.

λ.	λ/l.	E.	$\delta E/E$.
+ 0.16 cm.	+ 0.0040	18.80×10^{11}	− 0.016
+ 0.07 "	+ 0.0018	18.92	− 0.009
+ 0.06 "	+ 0.0015	18.98	− 0.006
+ 0.06 "	+ 0.0015	19.03	− 0.004
+ 0.04 "	+ 0.0010	19.07	− 0.002
− 0.03 "	− 0.0007	19.16	− 0.003
− 0.05 "	− 0.0012	19.02	+ 0.004
− 0.09 "	− 0.0022	19.30	+ 0.010
− 0.10 "	− 0.0025	19.30	+ 0.011
− 0.17 "	− 0.0042	19.42	+ 0.017
− 0.005 "	− 0.0001	19.10	.0092

It will be observed (*a*) that the highest value of λ obtained is only one third of 0.48 cm. required for the W.E. forks by Mercadier's empirical relation $\lambda = 0.012\ l$, (*b*) that the values are fairly evenly distributed on the two sides of zero, and (*c*) that their algebraic sum differs from zero by an amount which falls within the experimental errors of the measurement of the lengths of the prongs. Therefore the unmodified equation (3) gives closer results for the W.E. forks than Mercadier's equation (3′).

XI. The Modulus of Elasticity and Velocity of Sound in Steel.

Replacing v in equation (1) by its expression in terms of the modulus of elasticity E and the density ρ we have

$$P = \frac{4\pi\sqrt{3}}{r^2}\frac{l^2}{a}\sqrt{\frac{\rho}{E}}. \qquad (4)$$

Putting in the last equation 1.87011 for r, 7.363 for ρ and the values of P, l, and a obtained from the ten W.E. forks the values of E given in the third column of Table V. were obtained. The value 7.363 for ρ was obtained from a careful determination of the density of four pieces which were cut off the ends of the prongs of different forks in adjusting their periods. Using this value of ρ and the average value of E given at the bottom of the third column, the value 5.093×10^5 cm. per sec. was obtained for the velocity of sound in steel.

The deviations of the values of λ and of E from their mean values are small and undoubtedly due to the facts that (*a*) the prongs were not as uniform as might have been reasonably expected, and that (*b*) some of the forks were cut in more at the shoulders than others.

XII. TEMPERATURE COEFFICIENT OF MODULUS OF ELASTICITY OF STEEL.

Let P_0, a_0, l_0, ρ_0 and E_0 denote the values at 0° C. of the quantities involved in equation (4), and P, a, l, ρ *and* E denote their values at any other temperature t, then we can write

$$\frac{P}{P_0} = \frac{a_0}{a} \cdot \frac{l}{l_0} \cdot \left(\frac{\rho}{\rho_0}\right)^{1/2} \left(\frac{E}{E_0}\right)^{1/2}. \tag{5}$$

Introducing in the last equation the temperature coefficients α, θ, and ϵ defined by

$$l = l_0(1 + \alpha t),$$
$$P = P_0(1 + \theta t),$$
$$E = E_0(1 + \epsilon t),$$

we obtain, to a first order of approximation, the relation

$$\theta = -\frac{\alpha + \epsilon}{2},$$

or

$$\epsilon = -(2\theta + \alpha). \tag{6}$$

Since α and θ are both positive magnitudes ϵ, the temperature coefficient of the modulus of elasticity must be negative. In other words the modulus of elasticity decreases with increasing temperature. Taking the coefficient of linear expansion of steel to be 1.1×10^{-5} and substituting in equation (6) the values of θ given in the second column of Table I. we obtain the figures of the third column for the values of ϵ corresponding to the temperatures given in the first column. The variation of ϵ with the temperature is shown graphically by curve *II* of Fig. 12. The unmistakeable increase of the absolute value of ϵ with the increase of temperature indicated by Table I. and curve *II* is in agreement with results obtained by Pizati[9] and Dodge.[10]

The relatively large differences among the values of ϵ obtained by different observers must be due to the variety of the specimens of steel used and also due to experimental errors. It may be stated that the indirect method used in this paper is more accurate than the more direct methods by which the other observers have determined the temperature coefficient of elasticity.

In conclusion the author wishes to acknowledge his indebtedness and express his thanks to Professor W. F. Magie for placing the facilities of the Palmer Physical Laboratory at his disposal; to Professor E. H. Loomis for helping him place the constant temperature plant in working order; to Professor H. N. Russell for the use of the observatory chrono-

TABLE VI.

Observer.	$-\epsilon$.	Observer.	$-\epsilon$.
Wertheim[1]	2.8×10^{-4}	Gray, etc.[7]	2.47×10^{-4}
Kohlrausch & Loomis[2]	4.6	Wassmuth[8]	2.64
Pizati[3]	1.95	Walker[9]	2.5
Mayer[4]	2.21	Dodge[10]	1.9
Miss Noyes[5]	3.4	Dadourian	2.79
Shakespeare[6]	3.87		

graph; and to Captain H. B. Williams, who had charge of the sound ranging work of which the present investigation formed a part, for his interest in the work.

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[1] Wertheim, Pogg. Ann., 2, p. 1, 1848.
[2] Kohlrausch & Loomis, Pogg. Ann., 141, p. 481, 1870.
[3] Pizati, Nuo. Cim., 1, p. 181; 2, p. 137, 1877; 3, p. 152, 1879; 5, pp. 34, 135, 145, 1879.
[4] Mayer, Brit. Assoc. Rep., p. 573, 1894.
[5] Miss Noyes, PHYS. REV., 3, p. 433, 1896.
[6] Shakespeare, Phil. Mag., 47, p. 539, 1899.
[7] Gray, Blyth and Dunlop, Proc. Roy. Soc., 67, p. 180, 1900.
[8] Wassmuth, Phys. Zeits., 6, p. 755, 1906.
[9] Walker, Proc. Roy. Soc. Edin., 28, p. 562, 1907.
[10] Dodge, PHYS. REV., 5, p. 373, 1915.

THE MATHEMATICAL STRUCTURE OF BAND SERIES II.

BY RAYMOND T. BIRGE.

SYNOPSIS.—In the first article of this series, the author proposed a hyperbolic formula, for the accurate representation of long band series. The present paper initiates a more general discussion of this formula, and of the experimental results which the author has since obtained.

Detailed analytic work has shown the new formula accurate, within limits of experimental error, for those band series showing the most radical deviations from the simple Deslandres' law. Preliminary work indicates that the hyperbolic formula is equally satisfactory in the case of series showing positive deviations from Deslandres' law, instead of the customary negative deviations.

A complete investigation of any band series is greatly facilitated by a preliminary study of its deviations from Deslandres' law. New methods have accordingly been developed for making this comparison in a rapid, yet accurate manner. In particular, there is developed a new Least Squares' formula, giving directly the value of the only desired constant in a Deslandres' formula, thus avoiding the more extended calculations necessary when all three constants are simultaneously evaluated.

A comparative study of band and line series formulæ suggests for band series a modified hyperbolic formula. This modified formula has been tested on several series and has been found very satisfactory. New line series formulæ are also suggested, but are not seriously recommended at this time.

INTRODUCTION.

IN the first paper on this subject,[1] there was proposed a new formula for band series, together with the detailed quantitative results for the main (A_1) "singlet" series of the 3883 CN. band. It was shown also that preliminary work indicated that the formula would hold equally well for the other series of this band. In particular, the singlet series from the third head (C_1 series) exhibits the most radical deviations from Deslandres' law of any known band series. It therefore forms a crucial test for any new formula. This series has since been extended at both ends, the new lines having been identified from the author's own spectrograms. The complete quantitative results for this series were presented to the American Physical Society at the October, 1917, meeting.[2]

Certain remarkably systematic irregularities in the C_1 series, brought out by these computations, made it seem desirable to study also the B_1 series. This work has now been completed, much of the actual computing

[1] Astrophysical Journal, 46, 85–103, 1917. In the future, it will be referred to as I.

[2] PHYS. REV., (2), 11, 136, 1918.

having been done by an assistant, for whose services the author is indebted to the Rumford Committee of the American Academy of Sciences. At the same time, a general survey was made of practically all band series which seemed to show large deviations from Deslandres' law. A very considerable amount of material, both quantitative and qualitative, has now been collected, and it has seemed desirable to present a general review of the progress of the work to date. Such detailed results as appear of sufficient importance will be published later.

The present communication includes:

1. A discussion of methods of handling band series formulæ, in particular, Deslandres' parabolic formula.

2. A new viewpoint as to the original hyperbolic formula, together with a possible alternative formula in which the necessity of making a summation is avoided.

In the next paper there will be presented a review of typical band series, especially of those showing radical deviations from Deslandres' law, in a positive, as well as in a negative sense.

THE MATHEMATICAL ANALYSIS OF BAND SERIES.

It is well known[1] that all band series seem to conform to Deslandres' law[2] for at least an initial portion of their extent. The investigations of the author have convinced him that *no* band series strictly obeys Deslandres' law over *any* portion of its extent. But for short series (*i. e.*, series covering a small frequency interval) the deviations from this law may easily be far less than the experimental errors.[3] The first step however in the examination of any given series consists in determining how closely it conforms to the simple Deslandres' formula. Various methods for doing this have been used by previous investigators, but no general discussion of the matter has yet been published.

Deslandres' formula, in its original form,[4] states that the frequencies of successive lines of a band series are given by the parabola

$$\nu = \nu_0 + am + bm^2 \qquad (1)$$

or

$$\nu = A + B\,(m + c)^2, \qquad (1')$$

[1] For the most complete summarized description of all bands discussed in this series of articles, see Konen, "Das Leuchten der Gase und Dämpfe," pp. 199–278.

[2] Deslandres, Comptes Rendus, 103, 375, 1886.

[3] It may be remarked in passing that the amount of deviation from Deslandres' law seems to have no connection with the spectral extent of the series, nor with the number of terms in the series. Some series of 100 or more terms show a scarcely perceptible deviation, others of the same length a most radical deviation. Many series of few terms (30 or less) but of large spectral range also show radical deviations.

[4] For discussion see I., pp. 86–87.

where m takes successive integral values 0, 1, 2, 3, etc.[1] The successive first frequency differences are then given by the straight line

$$\Delta\nu = a + 2bm = 2B(m + c), \tag{2}$$

where m has the successive *fractional* values 0.5, 1.5, 2.5, etc., while the second frequency differences are given by the constant

$$\Delta\rho = 2b = 2B. \tag{3}$$

Any series for which the second frequency difference is constant therefore, per se, obeys Deslandres' law, and the first obvious method of testing this law is to compute these second differences.

But because of experimental errors, true perturbations, etc., these differences will never be constant, and in many cases it is difficult to tell from mere inspection whether they exhibit any definite trend from constancy. A far more delicate method of detecting any such trend, if present, is to plot the first frequency differences against m, on a fairly large scale. (50 × 50 cm. is recommended.) This curve, by Deslandres' law, should be a straight line, of slope $2b$ (*i. e.*, secondary frequency difference), and intercept ($\Delta\nu = 0$) $m = -a/2b = -c$. The author has called it the "slope" form, and has found it to be actually an hyperbola.

In practically all long series the slope curve exhibits a very definite trend from linearity. Yet in instance after instance investigators have analytically fitted the series to a Deslandres' formula, and have concluded that the agreement was satisfactory, when the slope curve (*if* it had been plotted) would instantly have shown the falsity of such a conclusion.

But let us assume that a casual inspection of the $\Delta\nu : m$ curve does not indicate any definite non-linearity. This condition is more likely to arise when the experimental errors are rather large (over 0.02 A). A case in point is the main series of the 3371 Nitrogen band, which Lewis[2] extended, by using self-induction in the circuit, until it entered the next band at 3159 A. The $\Delta\nu : m$ curve for this band is apparently a straight line and the equation given by Lewis is the best obtainable when the simplified Deslandres' formula

$$\nu = A + Bm^2 \tag{4}$$

[1] Comparing (1) and (1′) $b = B$; $c = a/2b$; $\nu_0 = A + Bc^2$. There seems to be some confusion as to just what is to be considered the "head" of a band. The ordinary idea, stated implicitly if not explicitly, is that this head is given by the line corresponding to $m = 0$, in any satisfactory formula. The author has tried in I. to follow consistently this usage. But (1′) is often written $\nu = \nu_0 + B(m + c)^2$. This makes ν_0 (the head) correspond to $m = -c$. I doubt if anyone actually thinks of the head in that way, and so the form is objectionable. Of course when $c = 0$, the two view-points become identical.

[2] Astrophysical Journal, 40, 148, 1914.

is used. As has been remarked[1] (4) is *not* Deslandres' law, and its use is permissible only when the inaccuracy of the data makes the true determination of the intercept ($-a/2b = -c = -$ "the phase") impossible. In this case, the data *are* rather inaccurate, but a slight improvement can be made by using (1′) rather than (4).

The problem now becomes,—what is the best analytical method of handling the experimental data, in order to determine whether or not the Deslandres' formula holds, *i. e.*, whether a straight line is really the best simple smooth curve that can be passed through the experimental points of the $\Delta\nu : m$ plot, and if so, what is the slope of this curve? This problem is identical with that of determining the constancy of the acceleration of gravity, and its value, if constant, given the position of a series of crests on an Atwood's Machine curve, but with the time and point of initial descent not known. For this latter problem we have

$$s = s_0 + \nu_0 t + 1/2gt^2 \tag{5}$$

or

$$s = (s_0 - \nu_0^2/2g) + g/2(t + \nu_0/g)^2, \tag{6}$$

i. e.,

$$s = \alpha + \beta(t + \lambda)^2, \tag{6'}$$

where λ = the "phase," *i. e.*, the fractional part of a second before $t = 0$ at which descent began.[2] In the case of Deslandres' law, (1) and (1′) correspond to (5) and (6′) respectively.

If a study of the actual plotted data, together with a knowledge of the experimental conditions, indicates that the deviations of the data from any simple smooth curve are due solely to chance experimental errors, then the method of Least Squares leads to the "most probable" values of the constants of the equation of the curve. In the case of spectral series, the conditions necessary for the legitimate application of Least Squares are actually present,—*i. e.*, in a well-measured series, using the new International standards, there is practically no opportunity for unsuspected systematic errors of any appreciable amount.

The full details of the method of Least Squares, as applied to the Deslandres' formula, are given by V. Carlheim-Gyllensköld.[3] The necessary calculations are, however, rather extended, especially in the case of long series. Moreover we do not, at the outset, wish to assume the truth of Deslandres' law. Instead, we wish to investigate whether or not the

[1] I., p. 89.

[2] I. e., we assume $t = 0$ for the nearest even second to the time of starting, just as in band series we choose m so as to make c (the "phase") some fraction less than 0.5. This may possibly be the analogy Thiele had in mind when he called c the "phase." The question of the origin of the term has recently been raised. (Proc. Phys. Soc. of London, 30, 130, 1918.)

[3] Svenska Vet. Ak. Handl., 42 N : r 8, 1907.

best smooth $\Delta\nu : m$ curve has a constant slope or a varying slope. But in the case of a long band series, such as the 3371 N series, the method of Least Squares can be applied, with great advantage, to this problem as well. For we may break up the $\Delta\nu : m$ curve into several sections, and determine, by Least Squares, the most probable value of the slope for each section. With 30 or more lines to a section, the probable error of this procedure is far less than that of any graphical method,—a fact which is frequently overlooked, but which the present series of investigations has repeatedly demonstrated.

The author has tried also various approximate methods for computing the second difference and of testing its constancy, but has come finally to the conclusion that the Least Squares solution is the only really feasible procedure in a case like that under consideration, where a plotted $\Delta\nu : m$ curve does not definitely indicate any curvature. Fortunately however it has been possible to very considerably reduce the amount of necessary calculations, so that the Least Squares method becomes but slightly longer than various approximate methods.

In equation (1) we have three undetermined coefficients, but in this particular case, we are interested only in the value of b. Moreover, the variable m takes on the regular series of values 1, 2, 3, etc. Now in the case of the simpler equation

$$y = A + Bx \tag{7}$$

it is possible to compute directly, by Least Squares, the value of B, when $x = 1, 2, 3, \ldots, n$. In fact[1]

$$B = \frac{(n-1)(y_n - y_1) + (n-3)(y_{n-1} - y_2) + , \text{ etc.}}{1/6n(n^2-1)}. \tag{8}$$

The "physical meaning" of (8) is that we are to combine the first and last observations, the second and next to last, etc., and each difference thus obtained is to be multiplied by a factor equal to the length of the interval (in terms of the corresponding change in x). Finally, we divide the numerator by the total number of corresponding changes in x. Thus for 6 observations, (8) can be written

$$B = \frac{5(y_6 - y_1) + 3(y_5 - y_2) + (y_4 - y_3)}{5^2 + 3^2 + 1^2}. \tag{8'}$$

In the case of equation (1), it is to be expected that a similar formula for the value of b can be derived. But so far as the author has been able to ascertain, no such formula has been published. Accordingly this work has been carried out, and the desired expression obtained. As is to be

[1] See Kohlrausch, "Physical Measurements," p. 17 (English translation of 7th German edition).

expected, the necessary reductions and the final result are much more complicated than in the case of (7) and (8). This result is

$$b = \frac{30}{n(n^2-1)(n^2-4)} \Sigma\{(y_r+y_{n+1-r})(A+[r-1]B+6[r-1][r-2])\}, \quad (9)$$

where $A = (n-2)(n-1)$,
$B = 6(2-n)$,
n = number of observations (y) [$y = v$ of (1)],
$r = \begin{cases} 1, 2, 3, \ldots n/2 \text{ for } n \text{ even.} \\ 1, 2, 3, \ldots (n+1)/2 \text{ for } n \text{ odd.}^1 \end{cases}$

Thus for $n = 6$, we have

$$b = \frac{5(y_6+y_1)-(y_5+y_2)-4(y_4+y_3)}{56}. \quad (9')$$

For $n = 5$

$$b = \frac{2(y_5+y_1)-(y_2+y_4)-2(y_3)}{14}. \quad (9'')$$

The "physical meaning" of (9) is this: The coefficients of the first and last observations, the second and next to last, etc., are the same. Hence the readings may be combined in pairs, as in the case of (8). (But note that the pairs of observations are added while in (8) they are subtracted.) The successive coefficients of these pairs of observations follow a parabolic law, in which the second difference is constant (= 12). Hence the calculation of the coefficients is very simple. In (9) A is the initial coefficient, and B the initial first difference. Thus formula (9) may be written

$$b = \frac{30}{n(n^2-1)(n^2-4)} \{A(y_1+y_n) + (A+B)(y_2+y_{n-1}) + (A+2B+12)(y_3+y_{n-2}) + (A+3B+36)(y_4+y_{n-3}) + , \text{etc.}\}. \quad (10)$$

In applying (9) to the N3371 series, the 84 observed frequencies (all weighted equally) were divided into two equal sets. For the first 42 (small m's) we obtain $b = 3.681$; for the second 42 (large m's) $b = 3.605$.[2] The mean is 3.643, very close to Lewis' value of 3.634, using the simplified equation (4).

Because of the large number of observations, the probable error in these results is very small. There is thus clear evidence of a variation

[1] Note that for n *odd*, the last term in the summation contains but *one* y, *i. e.*, $y_{n+1/2}$ with the coefficient $(1-n)(1+n)/2$.

[2] The best approximate methods which the author has been able to devise give for the first 42, $b = 3.645$ or 3.660; for the last 42,—3.585 or 3.555,—showing the uncertainty of the methods.

of slope of about 2 per cent. But since 3.681 is the probable slope at the center of the first half of the series, while 3.605 applies to the center of the second half, we have a probable total variation, over the entire extent of the observations, of about 4 per cent. It is thus evident that the second difference *decreases*, and that the series shows deviations from Deslandres' law in the *negative* sense. Moreover, we have thus detected this 4 per cent. variation in a case where a really good analytic fitting of Deslandres' formula reveals practically no trace of systematic deviations. Even when such deviations *do* appear in the analytic work, they are difficult to interpret. This 3371 series has been used for illustration because it is the only really long series, among those studied, which from the plotted $\Delta\nu : m$ curve *seemed* to obey the parabolic law.

In the case of more complex formulæ, such as the hyperbolic law proposed by the author, it is practically necessary to use the ordinary methods of calculation. After plotting the data and drawing the best smooth curve through the results, a number of points on this curve, equal to the number of arbitrary constants in the assumed formula, are chosen and the theoretical curve is made to pass through these points, by solving the simultaneous equations of condition. The Obs-Calc value for each observation is then calculated and plotted (as ordinate). A smooth curve is drawn through the results (the so-called "Residual Plot" [1]). The object is then to "warp" the x-axis until it fits this smooth curve as well as possible. With practice one can predict roughly whether it is possible to so warp the axis as to give a really good agreement. The criteria depend entirely upon the form of equation used, and general rules cannot be given. Each warping means, of course, the determination of a new set of constants. In the case of the hyperbola, four trials are usually sufficient, if the data are all equally trustworthy. For the B_1 and C_1 series of the 3883 CN band, many more trials were necessary, since the systematic deviations, to be discussed later, made it difficult to determine, at first, just what would constitute the best agreement. Much time was thus lost trying to do (in the light of future knowledge) quite impossible things.

Also, the hyperbolic formula refers to the $\Delta\nu : m$ curve. The Obs-Calc values are however calculated and plotted for the $\nu : m$ curve. The warping of the x-axis of the Residual Plot then consists in giving it a definite new *slope* (*i. e.*, a definite new $\Delta\nu$) at selected points, and solving, instead of giving it a definite new *ordinate*. The judging of the proper slope is far more difficult than the judging of the proper ordinate, and this is the one real objection to the use of the "slope" form of the equa-

[1] Goodwin, Precision of Measurements, p. 60.

tion. But the greater simplicity of this form more than compensates. The fact that, for the proposed hyperbolic formula, the $\nu : m$ equation is a summation, instead of an integral, is an objection to this particular formula but not to the use in general of the $\Delta\nu : m$ curve, rather than the $\nu : m$ curve.

THE HYPERBOLIC FORMULA, AND A POSSIBLE ALTERNATIVE FORM.

As shown in Fig. 2, page 92 of I., the $\Delta\nu : m$ curves[1] for the A_1, B_1, and C_1 series of the 3883 CN band look very much like hyperbolæ, instead of the straight line demanded by Deslandres' formula. These three series have now been found to fit accurately hyperbolic curves, save for certain systematic perturbations (previously known) and for small systematic irregularities, newly discovered. These latter amount to a change of frequency of only one part in 300,000 as a *maximum*, and so are inconsequential as far as the general form of the curve is concerned. Aside from the real periodic irregularities, the observed and computed curves agree to at least 0.005 A throughout a series 200 A long, *i. e.*, on a $\nu : m$ curve extending ten feet in each direction, the agreement is to less than 0.1 mm. throughout, indicating the great accuracy of the hyperbolic formula.

The deviations from Deslandres' law in all of these series are in a *negative* sense, in that the successive frequency differences increase *less* rapidly than demanded by the law, *i. e.*, the second differences *decrease*. Series of this type will be referred to as *negative series*, and bands containing them as "bands of the negative type." The phrase "negative bands" is already in use, with a distinctly different meaning. In I. the statement was made that in only one band are series known in which the deviations are in a contrary sense, *i. e.*, the 2370 band of air. This statement is quite incorrect. At the time of discovery, these 2370 series *were* the only known examples of what we shall call *positive series*. Since then a number of similar series have been found. It is these series which the author has been particularly studying. In the 2370 band there are four

[1] In all detailed quantitative work, the author has used the frequency in vacuo, but for the qualitative work to be described in the following paper the reduction to vacuo is not necessary and has not been made. Wave-lengths should never be used, except incidentally. In this connection it might be added, since it seems not known everywhere, that there is published a table of reciprocals (Cotsworth's Reciprocals,—McCorquodale and Co., London.) giving to seven figures the reciprocals of all numbers to 100,000. By linear interpolation to hundredths one can obtain the reciprocal of any 7 figure quantity to seven figures. The maximum error is one unit in the last figure, the probable error considerably less than half a unit. The rule for interpolating the seventh figure, as given in the tables, is obviously incorrect. The author has found it more convenient to use a slide rule for all interpolations. When a succession of adjacent frequencies is desired, as in a band series, each can be obtained in a very few seconds,—quite as rapidly, in fact, as by the use of the best calculating machines.

positive series, and four negative series. We shall call such a band a "*neutral band.*" At present the 2370 band is I believe the only known example.

In the only detailed study of this band,[1] a very good drawing but no data on the observed wave-lengths are recorded. (Schniederjost[2] resolves only a few lines of this band.) The only data given are the Obs-Calc values for every fifth line, for four of the series, together with the equations used. With this data it is possible to work back to the observed frequencies, for every fifth line, and thus to determine roughly the form of the $\Delta\nu : m$ curves. These curves show but slight deviations from a straight line, the maximum variation in slope being about 9 per cent. (for the II_2 and IV_2 series). That is, the final slope (highest m) is about 109 per cent. or 92 per cent. respectively, of the initial slope (at $m = 0$). The $\Delta\nu : m$ curve for the A_1 series of the 3883 band has been given in Fig. 2 of I. (page 92) and for convenience in comparing other series the slope at various points, in terms of the initial slope (*i. e.*, the relative second frequency differences) is given herewith.

$m =$ 0	100	per cent.	$m =$ 101	76.5	per cent.
21	98	per cent.	121	61.5	per cent.
41	95	per cent.	141	29.0	per cent.
61	91	per cent.	151	14.0	per cent.
81	85.5	per cent.	156.5	0	per cent. (max. $\Delta\nu$)

In respect to the magnitude of the departure from Deslandres' law, the 2370 series are thus not in a class with the 3883 series, or with many others studied, and the fitting of them to a six constant equation, such as that proposed by the author, would be a simple matter. The striking point about these 2370 series is however the fact that four of them show positive deviations, and four negative, and the deviations in corresponding series are *equal*. This shows that if the *negative* series are hyperbolic (and the $\Delta\nu : m$ curves look quite similar to the initial portion of the A_1 3883 curve) the *positive* series are *also* hyperbolic. It also suggests a new point of view on the entire subject.

We have assumed in I. that the hyperbolic law is due to the fundamental field of force of the molecule (all spectroscopists now agreeing that band series are due primarily to molecular structure, rather than to atomic). Let us assume however that the *tangent to the* $\Delta\nu : m$ *curve at* $m = 0$ represents this fundamental field of force, *i. e.*, a Deslandres' law, and that the deviations from this straight line indicate disturbing effects. Let us denote any $\Delta\nu$ on the straight line by $\Delta\nu_s$ and any $\Delta\nu$

[1] Deslandres and Kannapell, Comptes Rendus, 139, 584, 1904.

[2] Zeitschrift für wiss. Photographie, 2, 265, 1904.

on the hyperbola by $\Delta\nu_n$. Let $\Delta\nu_s - \Delta\nu_n = D$. Then if the $\Delta\nu_n : m$ curve is truly an hyperbola, the $D : m$ curve will also be an hyperbola (and conversely) since we have made only a linear transformation of variables in which the derivatives $ab - 4c^2$ remains invariant. (The transformation is mathematically the same as that from fixed to moving axes.) Moreover, the curve in $-D$ and m is also an hyperbola, by symmetry, and thus the curve in $\Delta\nu_s - (-D) = \Delta\nu_p$ is an hyperbola. (The converse transformation of variables.) Thus the four *positive* series ($\Delta\nu_p : m$ curves) are hyperbolæ, if the four *negative* series ($\Delta\nu_n : m$ curves) are. Also, we can state that the systematic deviations (D) from the fundamental field of force of the molecule (assumed to be such as to give a Deslandres' law) are of such nature as to yield hyperbolic $D : m$ curves, instead of saying that the field of force is such as to yield hyperbolic $\Delta\nu : m$ curves. The two statements are actually only different ways of viewing the phenomena, for the physical facts are the same, in either case.

The chief use that has been made of the above ideas is in the handling of positive series. It is difficult to recognize the hyperbolic form, in such series, and I have therefore drawn the tangent at $m = 0$, reversed the deviations (D) from this line, and drawn the resulting curve, thus obtaining the corresponding negative $\Delta\nu : m$ curve. This curve, in all cases, has appeared to be hyperbolic, as nearly as could be judged by mere inspection. This procedure also gives a simple method of judging, in the case of positive series, how radical are the departures from Deslandres' law. In only one series (one of those in the 3064 water band) does the corresponding negative $\Delta\nu : m$ curve extend past the point of maximum $\Delta\nu$. In this one case it has about the extent of the A_1 3883 curve. Thus no positive series shows anything like the deviation of the C_1 3883 series.

The so-called positive series are thus found (qualitatively, at least) to be no exception to the hyperbolic law, but to represent simply *positive* hyperbolic deviations from Deslandres' law, instead of *negative* deviations. Needless to say, the structure of *positive* band series is somewhat different from that of *negative* series. The former has no point of maximum $\Delta\nu$ and no "tail." The remarks on page 101 of I. should therefore be considered as applying only to *negative* series.

The hyperbolic law proposed by the author has the form

$$\Delta\nu^2 + B\Delta\nu.m + Cm^2 + D\Delta\nu + Em + F = 0, \qquad (11)$$

where $F = 0$ for the A_1 3883 series.

Solving for $\Delta\nu$ we have

$$\Delta\nu = -Bm/2 - D/2 \pm \sqrt{\left(\frac{B^2 - 4C}{4}\right)m^2 + \left(\frac{BD}{2} - E\right)m + \frac{D^2}{4} - F}, \quad (12)$$

where m = 0.5, 1.5, 2.5, etc., and the negative sign before the radical is to be used. Then

$$\nu_m = \nu_0 + [\Sigma\Delta\nu]_{m=0.5}^{m=n-0.5}. \quad (13)$$

Since $\Delta\nu$ is given by an hyperbola we might write (13) as

$$\nu = \nu_0 + \Sigma \text{ hyperbola}. \quad (14)$$

As explained in I., pages 100–101, the best convergent series that approximates this function is probably

$$\nu = a + bm^2 - cm^4 + dm^6, \text{ etc.}, \quad (15)$$

which Kilchling[1] uses as an empirical formula, but which Ritz[2] derived on theoretical grounds.

The formal analogy between line and band series has frequently been pointed out. The approximate formula for line series (Rydberg) is

$$\nu = \nu_\infty - \frac{N_0}{(m + \mu)^2}, \quad (16)$$

or

$$\frac{N_0}{\nu_\infty - \nu} = (m + \mu)^2. \quad (17)$$

The approximate formula for band series is

$$\nu = A + B(m + \mu)^2 \quad (1')^3$$

or

$$\frac{\nu - A}{B} = (m + \mu)^2. \quad (18)$$

(18) and (17) have the same functional form, and hence the formal analogy, previously stated by various authors. The following suggestions however are believed to be mainly original.

There seem to be two possible methods of modifying the $f(m)$ occurring in (17) and (18), in order to obtain more accurate formulæ. (1) Compute successive differences, in (17) and (18). This gives

$$\Delta\left(\frac{N_0}{\nu_\infty - \nu}\right) = 2(m + \mu), \quad (19)$$

$$\Delta\left(\frac{\nu - A}{B}\right) = \frac{\Delta\nu}{B} = 2(m + \mu). \quad (20)$$

[1] Zeitschrift für wiss. Photographie, 15, 293, 1916.

[2] Ritz (Weiss) Comptes rendus, 152, 585, 1911, or Astrophysical Journal, 35, 75, 1912.

[3] Here, as explained, A is *not* exactly equal to ν_0 (the true head) but differs from it by Bc^2. In giving the formal analogy between line and band series, equation (1′) is usually written with ν_0 in place of A. But to avoid inconsistency, this has not been done here.

But the author has found that $\Delta\nu$ = hyperbola, instead of $\Delta\nu$ = straight line. By analogy we might expect for line series

$$\Delta\left(\frac{N_0}{\nu_\infty - \nu}\right) = \text{hyperbola.} \tag{21}$$

The other method is (2) Compute the square roots of (17) and (18). This gives

$$\sqrt{\frac{N_0}{\nu_\infty - \nu}} = m + \mu, \tag{22}$$

$$\sqrt{\frac{\nu - A}{B}} = m + \mu. \tag{23}$$

In the case of line series, this second procedure has always been followed. The $\sqrt{N_0/\nu_\infty - \nu}$ instead of being a straight line, is actually a much more complex $f(m)$. Nicholson[1] concludes that it must be some $f(m + \mu)$. Ritz uses $f(m) = m + a + b/m^2$. Hicks uses $m + a + b/m$. Nicholson,[1] in order to get accurate agreement for even the simple Helium series, has had to use

$$m + \mu + \frac{a}{m + \mu} + \frac{b}{(m + \mu)^2} + \frac{c}{(m + \mu)^3}.$$

But *possibly* this $f(m)$ is an hyperbola. By analogy we would have, for band series,

$$\sqrt{\frac{\nu - A}{B}} = \text{hyperbola,} \quad \text{or} \quad \nu = A + (\text{hyperbola}),^2 \tag{24}$$

where B has been incorporated into the hyperbola. By comparing (24) with (14) it is seen that we have thus replaced the summation by a square, and have thus greatly simplified the necessary calculations.

Formula (24) has been carefully tested on the A_1 and C_1 series of the 3883 band. It *seems* to fit these series almost as well as does (14). More trials might possibly result in an equally good agreement. If either the A_1 or C_1 series were slightly longer, it would be possible to decide definitely between the two formulæ. The C_1 series extends much further (in terms of curvature) than the A_1, but because of the greater size of the perturbations and other irregularities of the C_1 series, there is a greater uncertainty as to the best position of the theoretical curve. The two formulæ can be made to give practically identical results for small values of m, but not for larger values.

The methods of handling the two formulæ are quite different, but only the following brief statement will be made at this time. With formula (24) it is possible to handle the data directly in terms of ν and m.

[1] Proc. Roy. Soc., (A), 91, 255, 1915.

But since the computations necessary in solving six simultaneous equations are several times as extended as those necessary for five, the author has preferred to work with the hyperbola, *i. e.*, with the curve in $\sqrt{\nu - A}$ and m. Now the experimental values of $\sqrt{\nu - A}$ are indeterminate, since A is as yet unknown. In the case of line series [compare (22) with (23)] it is possible to determine ν_∞ with great accuracy, regardless of the type of function used. The same thing is roughly true for A in band series. Any simple formula, such as Deslandres', applied to the known smaller values of m, will give an approximate value of A. It is moreover known that the curve in $\sqrt{\nu - A}$ and m must approach linearity, with decreasing m, since all band series approach Deslandres' law in this region, and this curve is very sensitive to small changes in A, when m is small. It is thus possible to determine accurately the value of A, necessary to get even approximate linearity. All computations can be made with a 20-inch slide rule. It is not necessary to have a good agreement between the observed and computed $\sqrt{\nu - A} : m$ curves, for m small, since in this case a relatively large change in $\sqrt{\nu - A}$ produces a relatively small change in $\nu - A$. The converse is true for large values of m, so that in this region the observed and computed $\sqrt{\nu - A} : m$ curves must agree very exactly.

By using the above method, the time required to determine a given set of constants is the same for the two formulæ. But for the new formula the time required for testing the constants is far less, and this constitutes, with the old formula, the major portion of the work. Since either of the formulæ give practically satisfactory results for the 3883 series, it is immaterial which form is used, in testing other simpler series. But since the original form allows the data for the hyperbolic curve $(\Delta\nu : m)$ to be computed directly from the observations, this form has been used in all the general work to date. Each form has six coefficients, or five, if the hyperbola cuts the origin.

In lines series, by analogy, we would have instead of (22)

$$\nu = \nu_\infty - \frac{N_0}{(\text{hyperbola})^2}. \qquad (25)$$

The author has plotted the experimental curves, for certain well-known line series, in terms of $\Delta(N_0/\nu_\infty - \nu)$ and m, and also in terms of $\sqrt{N_0/\nu_\infty - \nu}$ and m. The hyperbolæ (if either of the curves are such) are reversed, compared to band series, approaching linearity for large values of m, while the vertex occurs near the origin.[1] Unfortunately, line series do not

[1] The limiting slope ($m = \infty$) equals *two*, for the first form, or *unity*, for the second, regardless of the equation used, and thus should be the same for all line series, if N_0 is truly a universal constant. (Rydberg Constant). In band series one finds a great diversity of nitial slopes and there is no such corresponding universal constant.

yield themselves to graphical methods, for if an error of 0.01 A in term $m = 2$ is represented by, let us say, 0.01 mm., an equal error in $m = 30$ may be represented by about 5 mm. or more.

The author is not prepared, at the present time, even to suggest the use of either (21) or (25) for line series. The present trend of line series work is to derive formulæ directly from theoretical considerations. Because of the recent success of such efforts, by the use of various modifications of the Bohr atom,[1] it does not seem desirable to introduce any new purely empirical formula. In the case of band series, we should expect, from theoretical considerations, a formula of the type of (14) rather than of (24), since any application of the quantum idea must involve a summation, implicitly if not explicitly.

Addendum.

The author has just received a reprint of a long paper by T. Heurlinger entitled "Untersuchungen Uber Die Struktur der Bandenspektra" (Lund, 1918). A small portion of Heurlinger's work duplicates work (unpublished) of the author. In general however the ground covered is different. Heurlinger is not primarily interested in a new type of formula. He uses simply the power series (15), or a modification, and compares the numerical constants, for the various series. His main object is to relate together all the series in any one band, or group of bands, and to thus formulate general rules regarding band structure. The paper contains several ideas on band structure, radically new, but very suggestive, and apparently supported by a large amount of experimental evidence. The author intends to discuss these ideas more fully in a future paper.

University of California,
December, 1918.

[1] See particularly H. S. Allen, Proc. London Phys. Soc., 30, 127, 1918. Vegard, Phil. Mag., 35, 293, 1918. Ishiwara, Proc. Math. Phys. Soc. of Tokio, (2), 8, 106, 1915; (2), 8, 173, 1915; (2), 8, 540, 1916; (2), 9, 20, 1917; (2), 9, 160, 1917.

THE PASSAGE OF PHOTOELECTRONS THROUGH METALS.

BY K. T. COMPTON AND L. W. ROSS.

SYNOPSIS.—Theoretical expressions are derived giving the rate of escape of photo-electrons from the surface of a thin metallic film as a function of its thickness. These expressions result from various assumptions regarding the probability of escape of an electron photoelectrically excited at a given depth within the metal.

The photoelectric currents from films of platinum and of gold of various thicknesses are measured for different wave-lengths of light, and the results are found to be consistent with the view that the average distance in any direction which an excited electron may move without losing its ability to escape is about $2.67\ (10)^{-7}$ cm. in platinum and $5.0\ (10)^{-7}$ cm. in gold, and that the probability of going a given distance without losing its ability to escape falls off exponentially with the distance. This average distance is shown to be independent of the initial kinetic energy of the electron. There is evidence that platinum is first deposited in a relatively unstable and electropositive state, and that it spontaneously changes into the ordinary stable form.

A critical discussion and comparison of methods of measuring film thicknesses shows that they may be relied upon if proper precautions are taken. Various interesting properties of these thin films are illustrated and discussed.

INTRODUCTION.—Ladenburg[1] was the first to prove that electrons, excited photoelectrically within a metal by ultra-violet light, may travel some distance through the metal before escaping from its surface. He deposited nickel electrolytically on glass, and showed that the photoelectric currents from the films increased with increasing film thickness up to about $2(10)^{-4}$ cm. This result was qualitatively confirmed by Rubens and Ladenburg,[2] who showed that the ratio of the photoelectric currents on the incident and emergent sides of a piece of gold foil was about 100 : 1, while the ratio of the incident and emergent light intensities was about 1,000 : 1.

In 1913, Partzsch and Hallwachs[3] published a criticism of the quantitative results of Ladenburg's measurements, and also made a theoretical and experimental study of the optical and photoelectric properties of thin metal films deposited on quartz. The theoretical treatment in the present paper is based on, and is an extension of, the work of Partzsch and Hallwachs.

The experimental measurements here recorded are in many respects

[1] Ann. d. Phys., 12, p. 558, 1903.

[2] Ber. d. D. Phys. Ges., p. 749, 1907.

[3] Ann. d. Phys., 41, p. 247, 1913.

similar to measurements published by Robinson,[1] and in the main confirm his results. Certain refinements had to be added to his experimental procedure, however, in order to attain sufficient accuracy to permit a quantitative application of the theory.

METHOD.—The general plan of the experiment was to allow ultraviolet light of definite wave-length to enter a metal film, deposited on a quartz plate, from the quartz side and to measure the total photoelectric emission from the film. This was done with films of various thicknesses, maintaining other conditions constant, so that the photoelectric emission was obtained as a function of the film thickness. The nature of the variation of emission with thickness depends on the distance rate of absorption of light in the film and on the probability that an electron, photoelectrically excited by the light at any point in the film, may reach and escape from the surface of the film. The rate of absorption of light in the film is known, or may easily be measured. Thus the experimental results depend ultimately on the probability of the escape of an electron from any point in the film. Various assumptions regarding the form of the expression of this probability, associated with various assumptions regarding the passage of electrons through the metal, may therefore be tested by the experimental results. In the following section several such assumptions are put into forms suitable for quantitative tests.

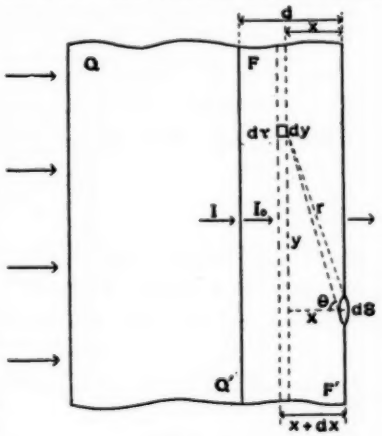

Fig. 1.

THEORY.—Let QQ' and FF' in Fig. 1 represent sections of the quartz plate and metal film, respectively, the thickness of the latter being d. Light of intensity I strikes the film from the quartz side, but part of it is reflected, so that I_0 represents the intensity of the light which enters the film. Since the reflecting power of the film varies with its thickness, I_0 is a function of d.

Let dx be the thickness of a layer of the film distant x from its free surface. The intensity of the light in this layer is $I_0\epsilon^{-\alpha(d-x)}$, where α is the coefficient of absorption of the light. If we let ν represent the number of electrons which are photoelectrically excited per unit time, per unit volume, per unit light intensity, then the rate at which electrons

[1] Phil. Mag., 25, p. 115, 1913; *ibid.*, 32, p. 421, 1916.

are excited in the layer dx is

$$\nu A I_0 \epsilon^{-\alpha(d-x)} dx,$$

where A is the area of the film. From symmetry it is evident that half of these start moving toward the free surface.[1]

Let $F(x)$ be the probability that an electron will move a distance whose component normal to the surface is x without losing its ability to escape. Then the rate of escape from the film of electrons which start from the layer dx is

$$dN = \frac{\nu A I_0}{2} \epsilon^{-\alpha(d-x)} F(x) dx.$$

The total rate of emission of electrons is therefore

$$N = \frac{\nu A I_0}{2} \epsilon^{-\alpha d} \int_0^d \epsilon^{\alpha x} F(x) dx. \tag{1}$$

SPECIAL CASES.—(*a*) *Assume that the number of electrons which retain ability to escape falls off exponentially with distance moved normally to the surface, or*

$$F(x) = \epsilon^{-\beta x}, \tag{2}$$

where $1/\beta$ is the average distance which an electron can move normally to the surface without losing its ability to escape. Then the integration in equation (1) is easily performed, giving

$$N = \frac{\nu A I_0}{2} \frac{\epsilon^{-\alpha d} - \epsilon^{-\beta d}}{\beta - \alpha}, \tag{3}$$

which is identical with the equation derived by Partzsch and Hallwachs.[2]

(*b*) *Assume that the number of electrons which retain ability to escape falls off exponentially with the distance moved (in any direction).*—Consider those electrons which start toward the surface from an element of volume $d\tau$ in the layer dx and escape from an element of the free surface dS. Of these, the fraction $dS \cos\theta/2\pi r^2$ start toward dS; but of these, only the fraction $\epsilon^{-\gamma r}$ succeed in escaping, according to our present assumptions. Thus

$$\frac{dS \cos\theta}{2\pi r^2} \epsilon^{-\gamma r}$$

[1] This assumes that the electrons begin to move with equal probabilities of motion in all directions and therefore in directions which are independent of the orientation of the electric vector in the light wave. There is possibly some experimental evidence that this assumption is not strictly true. If the electron is ejected from the atom by a direct pull from the electric field of the light wave the present assumption is probably seriously in error. If, however, the photoelectric emission is a secondary effect caused by a storing up of energy in the atom and its consequent instability, the assumption is valid.

[2] *Loc. cit.*

is the probability that an electron, starting toward the surface from $d\tau$, will escape from dS. It is to be noted that this probability is the same for electrons starting from any point in dx at a distance between y and $y + dy$ from O. Thus the probability that an electron, starting toward the surface from any point in the layer dx, will escape from dS is

$$\frac{1}{A}\int_{y=0}^{y=\infty}\frac{dS\cos\theta}{2\pi r^2}\epsilon^{-\gamma r}\cdot 2\pi y dy,$$

since the layer may be considered to extend to infinity in comparison with the depth x. Finally, the probability that an electron, starting toward the surface from dx, will escape, is found by substituting A for dS, and is

$$F(x) = \int_0^\infty \frac{\cos\theta}{r^2} y\epsilon^{-\gamma r}dy.$$

This expression may be written

$$F(x) = x\int_x^\infty \frac{1}{r^2}\epsilon^{-\gamma r}dr,$$

of which the solution is

$$F(x) = \epsilon^{-\gamma x} + \gamma x Ei(-\gamma x), \tag{4}$$

where $Ei(-\gamma x)$ represents the exponential integral

$$Ei(-\gamma x) = -\int_x^\infty \frac{1}{r}\epsilon^{-\gamma r}dr,$$

whose value for various values of (γx) is given in Laska's "Sammlung von Formeln."

On this assumption, therefore, the total rate of electron emission from the film should be, by equation (1),

$$N = \frac{\nu A I_0}{2}\epsilon^{-\alpha d}\int_0^d \epsilon^{\alpha x}[\epsilon^{-\gamma x} + \gamma x Ei(-\gamma x)]dx. \tag{5}$$

The integral of this expression may be easily evaluated by graphical methods.[1]

[1] This equation may be integrated by parts after substituting for $Ei(-rx)$ its alternative form given above. In performing this integration it is necessary to express the limits of integration of one of the terms by

$$\int_0^d f(x)dx = \int_0^\infty f(x)dx - \int^\infty f(x)dx$$

and to remember that

$$\int_0^\infty \frac{\epsilon^{-rz} - \epsilon^{-(r-a)z}}{z}dz = \log\frac{r-\alpha}{r}.$$

We thus find for the solution

$$N = \frac{\nu I_0 A}{2}\left\{\frac{1}{\alpha}(\epsilon^{-rd} - \epsilon^{-ad}) + r\left(\frac{d}{\alpha} - \frac{1}{\alpha^2}\right)Ei(-rd) + \frac{r}{\alpha^2}\epsilon^{-ad}Ei(-(r-\alpha)d) + \frac{r}{\alpha^2}\epsilon^{-ad}\log\frac{r}{r-\alpha}\right\}.$$

In this expression, $1/\gamma$ represents the average distance in any direction which an electron may move without losing its ability to escape.[1]

(*c*) *Assume that an electron loses energy in proportion to the distance moved through the metal.*—Let σ be the energy lost per centimeter path. The electron starts with an amount of energy $h\nu$, where h is Planck's constant and ν is the frequency of the exciting light; of this energy, an amount $h\nu_0$ is necessary to enable it to escape from the surface of the metal. Therefore

$$\sigma r_0 = h(\nu - \nu_0) \tag{6}$$

determines the greatest distance r_0 which an electron can move in the metal without losing its ability to escape. As in case (*b*), the fraction $dS \cos\theta/2\pi r^2$ of the electrons starting toward the free surface from $d\tau$ move toward dS. All these will escape if $r < r_0$, and none if $r > r_0$. Thus the probability that an electron starting toward the surface from the layer dx will escape from dS is

$$\frac{1}{A}\int_0^{\sqrt{r_0^2-x^2}} \frac{dS\cos\theta}{2\pi r^2}\cdot 2\pi y dy = \frac{dS}{A}\left(1 - \frac{x}{r_0}\right)$$

if $x < r_0$ and is zero if $x > r_0$. Therefore

$$\left.\begin{aligned} F(x) &= \left(1 - \frac{x}{r_0}\right) \quad \text{if} \quad x < r_0; \\ &= 0 \qquad\qquad \text{if} \quad x > r_0. \end{aligned}\right\} \tag{7}$$

By equation (1), if $d > r_0$,

$$\begin{aligned} N &= \frac{\nu A I_0}{2}\epsilon^{-\alpha d}\int_0^{r_0}\left(1 - \frac{x}{r_0}\right)\epsilon^{\alpha x}dx \\ &= \frac{\nu A I_0}{2}\epsilon^{-\alpha d}\left[\frac{1}{\alpha^2 r_0}(\epsilon^{\alpha r_0} - 1) - \frac{1}{\alpha}\right], \end{aligned} \tag{8}$$

Although this equation permits numerical computations to be made, such computations are neither as rapid nor as accurate as those made by a graphical solution of equation (5). The inaccuracy is due to the fact that the value for N is expressed as the *difference* between relatively large terms, and the tables of $Ei(-rx)$ are not sufficiently accurate to give the difference with high percentage accuracy.

[1] We have implicitly assumed that the "ability to escape" depends on the velocity but not on the direction of motion of an electron at the surface. This is objectionable, since the chance of escaping against the attraction of the induced positive charge left on the film is certainly dependent on direction as well as speed of motion of an electron. The mechanism of "escape" and the nature of the work done in escaping is so little understood, however, that we have neglected this factor. If most of the work done in escaping is done within distances from the surface which are of atomic order of magnitude, the present assumption will probably not be seriously in error. It can furthermore be shown that the relations between N, α and r are such as to reduce any error from this cause to a minimum.

and if $d < r_0$

$$N = \frac{\nu A I_0}{2} \epsilon^{-ad} \int_0^d \left(1 - \frac{x}{r_0}\right) \epsilon^{ax} dx$$
$$= \frac{\nu A I_0}{2} \left[(1 - \epsilon^{-ad}) \left(\frac{1}{\alpha} + \frac{1}{\alpha^2 r_0}\right) - \frac{d}{\alpha r_0} \right]. \tag{9}$$

Thickness of Film giving Maximum Photoelectric Emission.—It is much easier, in practice, to determine or test values of β, γ and σ by finding the thickness of film giving maximum emission than by attempting to fit the entire graphs of the theoretical equations to the experimental curves. We shall therefore discuss the conditions under which maximum emission is obtained in the three cases considered above.

(*a*) By equating to zero the derivative of equation (3) with respect to film thickness d we find the thickness d_m for maximum emission to be given by

$$d_m = \frac{1}{\beta - \alpha} \log \frac{\beta - \left(\frac{1}{I_0} \frac{\partial I_0}{\partial d}\right)_m}{\alpha - \left(\frac{1}{I_0} \frac{\partial I_0}{\partial d}\right)_m}, \tag{10}$$

in which the term $1/I_0 \, \partial I_0/\partial d$ arises from the variation of the reflecting power of the quartz-film surface with thickness and may be determined experimentally, as described later. Taking experimental values of this term and of the coefficient of light absorption α we find the values of d_m for various values of α and β shown graphically in Fig. 2. If d_m and α

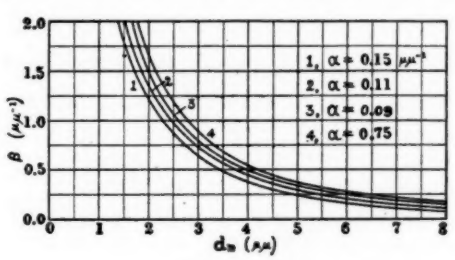

Fig. 2.

are determined experimentally, the appropriate value of β may be found from these curves.

(*b*) To find the maximum value of N from equation (5) the easiest method is to actually plot the equation, as is done in Fig. 3 for various values of γ.[1] From these and similar curves the values of d_m appropriate

[1] In Fig. 3 the curves for various values of r are drawn so as to merge into the curve giving the percentage of transmitted light, thus calling attention to the fact that for thick films the photoelectric emission varies with thickness in practically the same manner as does the transmitted light. To do this, however, the four curves had to be plotted to four different scales. If drawn to the same scale the maximum values of N for the four curves 1, 2, 3 and 4 would be 21.3, 39.9, 70.9 and 121.7 respectively.

to various values of γ and α have been determined and plotted in Fig. 4, whence γ may be found if α and d_m are experimentally determined.

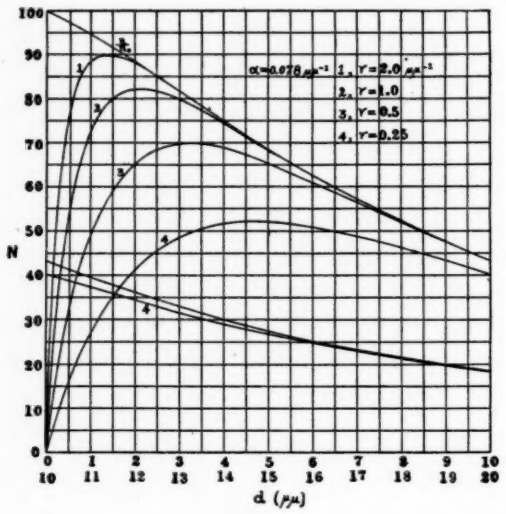

Fig. 3.

(*c*) In case energy is lost in proportion to the distance moved through the metal, the thickness for maximum emission is given by differentiation of equation (9), whence

$$d_m = \frac{1}{\alpha} \log (1 + \alpha r_0), \tag{11}$$

where r_0 is defined by equation (6) as the greatest distance which an electron can go through the metal without losing its ability to escape.

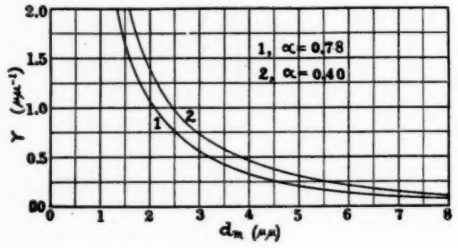

Fig. 4.

Since αd_m is an extremely small quantity, equation (11) may be written without appreciable error, $\alpha d_m = \alpha r_0$, whence, by equation (6)

$$d_m = \frac{h(\nu - \nu_0)}{\sigma}. \tag{12}$$

If this were the actual type of energy loss, the thickness of film giving maximum current should be proportional to $(\nu - \nu_0)$, which is the difference between the frequency of the exciting light and the least frequency of light which will produce photoelectric emission.

APPARATUS.—In order to test the foregoing assumptions and to measure some of the quantities involved, metallic films were deposited on quartz plates by the method of "sputtering," in a vessel whose essential features are shown by Fig. 5. Transparent quartz plates one centimeter square and one millimeter thick were carefully cleaned in boiling caustic potash, nitric acid and distilled water and mounted by a touch of sealing wax over holes in a brass disk, as at *P*. Twelve such plates were mounted on the disk, which was then placed in the vacuum chamber shown in Fig. 5, so that the plates could be placed in turn under the cathode *C* by turning the ground glass joint *J*. A stationary brass shield *SS'* was held just above the disk *NN'* so as to shield from the discharge all the plates except the one *P* below the cathode. The vessel was rendered air tight by melting wax in the groove *GG'*. Great care was taken to keep the inside of the vessel free from wax or grease, and where wax was necessary it was entirely shielded from the discharge. The exhaust tube was connected through a liquid air trap to a McLeod gauge and Gaede pump. The source of the discharge current was a Snook high potential transformer designed to give a very steady discharge.

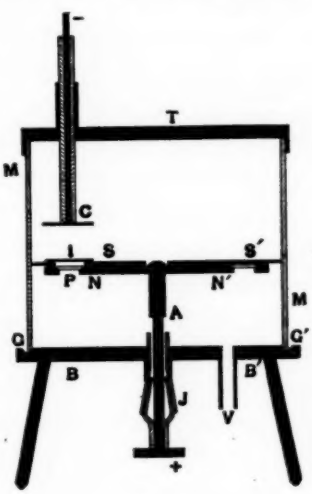

Fig. 5.

Measurement of Thickness of Films.—Three methods were employed to measure the thickness of the films. Of these, the most direct method was to weigh the thickest film, thence calculate its thickness and take the thickness of the other films proportional to their times of exposure to "sputtering." B. Pogány[1] has shown that this method is accurate if the sputtering conditions are maintained constant. In order to have constant conditions we adopted the following procedure. An iron disk *I* was placed over the hole in the shield *SS'* so that none of the quartz plates was exposed to the discharge. The discharge in the vessel was then continued for about two hours, until no more gas could be detected coming from the walls of the vessel under the influence of the discharge.

[1] Phys. Zeit., 15, p. 685, 1914.

Then the iron disk I was removed by a magnet and the plates were exposed successively to the discharge. They were exposed in the following order: 1, 2, 3, ···, 11, 12, 12, 11, ···, 2, 1, 1, 2, ···, 12, 12, ···, 1; so that the effect of any change in sputtering conditions would be evenly distributed among the plates. During the entire process the gas pressure was maintained constant by a regulating valve. Ordinarily, the times of deposit ranged from 1 minute to 100 or more minutes.

The second method employed involved a measurement of the absorption of light in the films. The disk NN' was mounted on an optical bench so that light from a mercury arc could be focused on any one of the films. The reflected or transmitted light was focused on the slit of a Hilger monochromatic illuminator provided with a linear thermopile, which served to measure the intensity of the light. By thus determining the intensity of the incident light, the reflection and absorption by the quartz plate and the intensities of the lights transmitted and reflected by the film covered plates, we found the fraction of the light entering the film which was absorbed by it. The coefficient of absorption of light of the wave-lengths used, 576.9 $\mu\mu$ and 579.1 $\mu\mu$, is accurately known, whence the thickness of each film could be calculated.

The third method involved the use of data concerning the variation of reflection of ultra-violet light with thickness of platinum films on quartz, published by Partzsch and Hallwachs.[1] When light strikes a platinum film from the quartz side, they found that the intensity I_0 of light entering the film is less than the intensity I of light incident on the quartz by an amount shown by curve 1, Fig. 6, for films of various thicknesses d. Ninety-two per cent. of the incident light is transmitted by a blank plate. From this we find that the ratio of the intensity of light transmitted by a blank plate to that transmitted by a plate with film of thickness d is given by

$$\frac{n}{n_0} = \frac{I_0}{.92}\epsilon^{-\alpha d}, \tag{13}$$

in which α is known with considerable accuracy for the wave-length 253.6 $\mu\mu$ as a result of a slight extra-polation of measurements made by Meier.[2] Taking $\alpha = .078\ \mu\mu^{-1}$, we obtain curve 2, Fig. 6. The intensity of the light transmitted by any film was taken to be proportional to the photoelectric current produced when this light fell upon a plate P (Fig. 7) which could be placed in the path of the light. The ratio of this current to that produced by light which has passed through a blank plate was therefore equal to n/n_0. Thus the thickness of the film d could be

[1] *Loc. cit.*

[2] Ann. d. Phys., 31, p. 1017, 1909.

found directly from curve 2, Fig. 6, as soon as the ratio n/n_0 was determined.

The reliability of these methods of estimating film thickness is proven by a comparison of their results when applied to the same set of films.

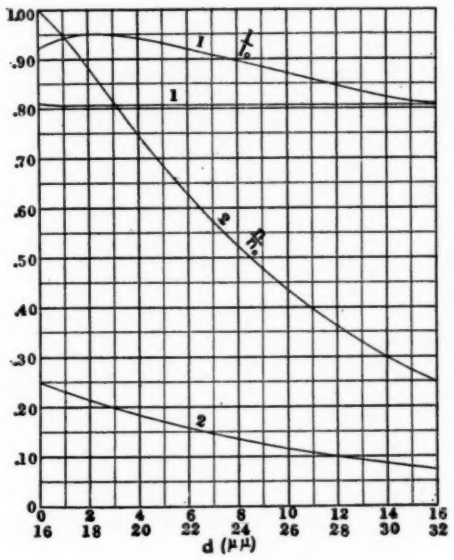

Fig. 6.

In Table I., t represents the time of sputtering and d_1, d_2, d_3 are the thicknesses calculated by the three methods, respectively. The area

TABLE I.

No.	t (sec.).	d_1(μμ).	d_2(μμ).	d_3(μμ).
1	0	0	0	0
2	20	1.5	1.8	1.7
3	30	2.3	2.5	2.5
4	40	3.1	3.0	3.0
5	50	3.8	3.8	3.9
6	60	4.5	4.4	4.6
7	70	5.3	5.5	5.5
8	80	6.0	6.5	6.2
9	90	6.8	6.8	6.6
10	120	9.0	8.6	8.6
11	150	11.3	11.8	11.6
12	6000	452.0	?	?

of plate no. 12 was 0.95 sq. cm. and the mass of film deposited on it was 0.000925 gm. This film was so opaque that no estimates of its thickness could be made by the second and third methods. The experimental

data which were used, with Curve 2, Fig. 6, to find the values of d_3 are found in Table II.

Of these methods, the third was most convenient, and was used for most of the work with platinum films. The data for its use in dealing with gold films are lacking, so that we employed the second method in this case.

Photoelectric Measurements.—The photoelectric properties of these films were tested in the brass vessel shown in Fig. 7. Electrical contact between the films and the brass disk NN' was made by gold leaf, cemented with a little India ink. The disk was mounted on a shaft A in such a manner that any film F could be placed in the path of ultraviolet light from a quartz mercury arc and a Hilger monochromatic illuminator. This light entered through a quartz window W, was brought to a focus at the slit S, passed through the quartz plate and film and entered the hollow brass box B. This box was designed to reduce the amount of light returning to the film after reflection from the box, and a calculation proved that less than one per cent. of the photoelectric current from the film could be due to light reflected from the box.

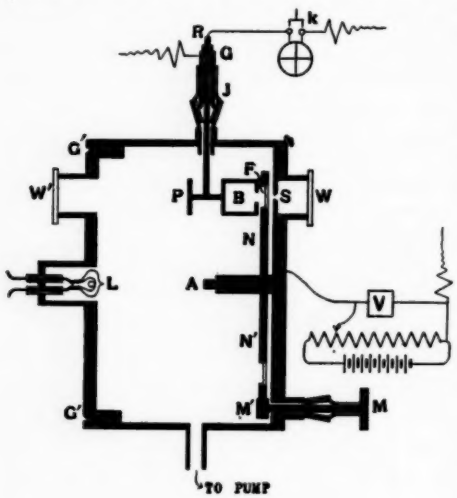

Fig. 7.

The photoelectric current N from the film F passed to the box B which served as the receiving electrode, and was connected with an electrometer which was used at a sensitiveness between 2,000 and 50,000 mm. per volt, depending on the type of measurement being made. The vessel and films were charged to a negative potential of about 10 volts, indicated by the voltmeter V, and the insulation of the electrometer system was protected by the guard ring G.

In order to measure the intensity of the light transmitted by the film, the platinum plate P was turned to the position of the box B and the potential of the vessel changed to + 10 volts, so that the electrometer measured the photoelectric current n from the plate.

To facilitate quick substitution of one film for another, a second toothed wheel M', which could be rotated by the outside handle M, was made to engage the toothed disk NN'. A small lamp L illuminated the

inside of the vessel, and the adjustment of any film to the position F was visible when looking through the window W'.

EXPERIMENTAL RESULTS. PLATINUM.—Ten sets of platinum films were tested, each set being examined to determine (*a*) the thickness of film giving maximum photoelectric emission, (*b*) the effect of using different wave-lengths of exciting light and (*c*) the nature of changes which occur in the films after they are deposited on the quartz plates. These points will be taken up separately.

(*a*) *The Thickness of Film Giving Maximum Photoelectric Emission.*—Table II. contains typical experimental measurements. The numbers

TABLE II.

No.	N_1.	N_2.	N.	n_1.	n_2.	n.	$d(\mu\mu)$.
1	0	0	0	191	186	188	0.0
2	47	45	46	170	168	169	1.7
3	74	68	71	162	158	160	2.5
4	83	82	82	153	152	152	3.0
5	81	81	81	145	139	142	3.9
6	77	72	75	134	131	133	4.6
7	67	68	67	122	124	123	5.5
8	65	62	63	117	113	115	6.2
9	67	67	67	112	112	112	6.6
10	58	60	59	92	93	93	8.6
11	31	29	30	71	71	71	11.6
12	0	1	1	0	0	0	?

in the columns marked N refer to the electrometer deflections per half minute due to the photoelectric currents from the films. Those marked n refer to currents from the plate P and measure the intensity of the light transmitted by the films; these data are used with Fig. 6 to determine the film thickness d. In order to avoid error due to "time" changes, such as photoelectric fatigue, all measurements were taken in order 1, 2, 3, $\cdots$, 11, 12 and back again 12, 11, $\cdots$, 2, 1, as shown in the columns marked with subscripts 1 and 2. The means of these measurements are given in columns N and n.

These results are shown graphically in Fig. 8 (*c*). It is seen that there are two maxima, instead of the one predicted by the theory. It might be thought that this is due to some erratic photoelectric condition of films 9 and 10, if it were not for the fact that they were found in every one of the ten sets of platinum films tested. Other examples are shown in curves (*a*), (*b*) and (*d*), in which the ordinates have been changed by constant factors in order to avoid confusion in plotting. It appears that there is one maximum at $d = 3.75\ \mu\mu \pm .25\ \mu\mu$ and another in the neighborhood of $d = 7.5\ \mu\mu \pm 1.0\ \mu\mu$.

Numerous tests were made in an attempt to discover the cause of the second maximum. For one set of films mercury vapor was allowed free access to the sputtering and testing vessels, while in other tests all parts were carefully cleaned and mercury vapor excluded by liquid air traps, but no difference was observed. Apparently it made no difference

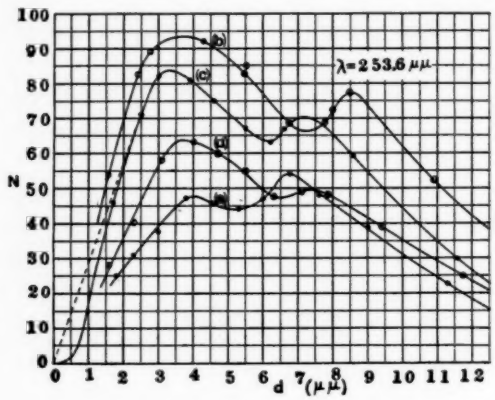

Fig. 8.

whether the films were allowed to stand in air or in *vacuo*. We have concluded that both maxima are really due to properties of the platinum films. The interpretation of these maxima is suggested by experiments discussed in the following sections.

One other feature of these curves is of interest. All the curves near the origin show an inflection, as if the photoelectric currents increased with thickness of film, first slowly and then more rapidly. If the quantity ν in our theoretical equations were constant, this portion of the curve would be straight, indicating proportionality between emission and thickness. Robinson,[1] who has noticed this phenomenon, has supposed that it indicates less intrinsic photoelectric sensitiveness for thin than for thicker films. We have been able to prove, however, that ν really is constant, and that the inflection in the curves is due to a secondary cause, viz., lack of continuity of very thin films. When a very thin film is first exposed to the ultra-violet light, the rate of electrometer deflection falls off rapidly as the exposure is continued. If the light is shut off the film regains its original apparent sensitiveness only after a lapse of some minutes. If the *initial* rate of deflection instead of the total deflection in a relatively long time interval is used to determine N, it is found that the values of N tend to lie on the theoretical straight line, such as the dotted line in curve (*c*). This is much more marked

[1] *Loc. cit.*

in the case of gold films than in the case of platinum films—which is in line with the observation that a greater thickness of gold than of platinum is required to give an electrically conducting layer.[1] The upward concavity of the curves near the origin is apparently to be explained, therefore, by the effect of isolated regions of the film which quickly charge up to such positive potentials as to reduce the rate of emission from these and contiguous parts of the film. This phenomenon is easily detected by the failure to get electrometer deflections which are proportional to time, but it was never observed in the case of a platinum film thicker than 2 $\mu\mu$.

(*b*) *The Effect of Using Different Wave-lengths of Exciting Light.*—The influence of the wave-length of exciting light upon the character of the emission is shown by the curves of Fig. 9. All show the double maximum,

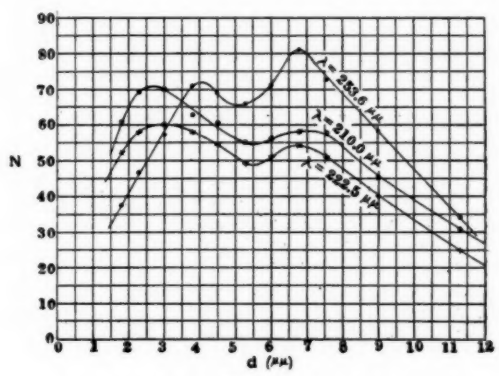

Fig. 9.

but there are two points of difference. The second maximum is relatively smaller and the first maximum is displaced toward the left when dealing with the shorter wave-lengths. Every set of films tested showed these characteristics, although they were more pronounced in some sets than in others.

(*c*) *Time Changes.*—An examination of Fig. 8 shows that even for a given wave-length, the two maxima are not always of the same relative magnitude. This is due to a slow time change in the properties of the films, an actual example of which is shown by Fig. 10. The second maximum becomes relatively less important as the film stands, and it makes no apparent difference whether the films stand in *vacuo*, or exposed to air. Heating the films in an oven at about 150° C., however, greatly accelerates the change, and after this treatment the second hump is scarcely noticable.

[1] King, PHYS. REV., 10, p. 291, 1917.

DISCUSSION OF RESULTS. *Interpretation of the Two Maxima.*—Apparently the two maxima of the curves must be ascribed to platinum in two conditions. Of these conditions, the one giving rise to the right hand maximum is evidently more unstable and more electropositive than the other, since it is relatively more important soon after the formation of the films and relatively more sensitive to light of long wave-lengths. We therefore take the first maximum to be characteristic of platinum in its ordinary stable state, while the second maximum is due

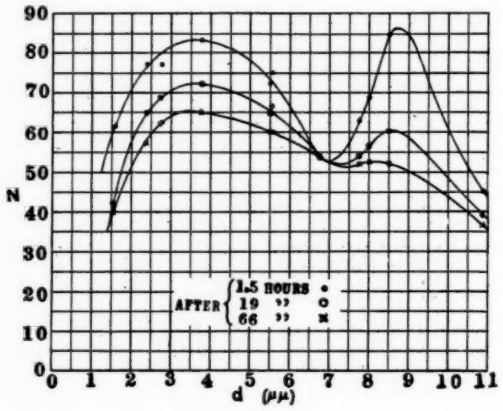

Fig. 10.

to platinum in the amorphous or spongy state in which it is first deposited. Since the change from the amorphous to the stable state is spontaneous, the latter state must be one of less internal potential energy, which is in accord with the observation that the platinum in this state is more electronegative. It is also seen, by reference to Figs. 2 and 4, that the average distance, $1/\beta$ or $1/\gamma$, moved by an electron without losing its ability to escape is greater in the less compact state. These deductions are all consistent with each other and are also in line with well known facts regarding the abnormal resistivity of freshly sputtered films and the change to normal resistivity produced by "aging." We shall therefore confine the remaining discussion to the information regarding ordinary platinum which is given by a study of the first maximum.

Comparison of the Three Assumptions Regarding the Process by which an Electron Loses its Ability to Escape.—The third assumption, viz., that an escaping electron loses energy in direct proportion to the distance traveled through the metal, may at once be discarded. According to it, the thickness giving maximum emission should be directly proportional to $(\nu - \nu_0)$ by equation 12, or to $(1/\lambda - 1/\lambda_0)$, where λ is the wave-length of the exciting light and λ_0 is the longest wave-length of light which will

cause photoelectric emission. λ_0 is known to be about 280 $\mu\mu$ for platinum.[1] The values of λ employed ranged from 210 $\mu\mu$ to 265 $\mu\mu$. Thus the assumption requires that d_m should be four or five times larger for the shorter than for the longer wave-lengths. Not only is this not the case, but what little variation of d_m with λ is found is in the opposite direction to that required by the assumption.

As far as we can see, either the first or the second assumptions are in conformity with the facts. We are unable to decide between them experimentally, since either equation (2) or equation (5) satisfies the experimental results within the limits of uncertainty introduced by the presence of the second maximum. Of the two assumptions, however, the more reasonable one is the second—viz., that the probability that an electron will retain its ability to escape decreases exponentially with the distance traveled from its starting point.

On this assumption, we may determine $1/\gamma$, the average distance which an electron may move without losing its ability to escape. For $\lambda = 253.6$ $\mu\mu$, we may take $d_m = 3.75$ $\mu\mu$ as the mean of all our determinations. Taking $\alpha = .078$ $\mu\mu^{-1}$, we find γ, from Fig. 4, to be 0.375 $\mu\mu^{-1}$.

For shorter wave-lengths, d_m has slightly smaller values. This may be due to a larger value of α for shorter wave-lengths or to a larger value of γ. This latter possibility is very unlikely, since it would mean that the rapidly moving electrons have less average penetrating power than the slow ones. We attempted measurements of α for the shorter wave-lengths and did succeed in proving that α increases as λ is decreased below about 245 $\mu\mu$, but our measurements were not accurate enough to prove that the shift of d_m with wave-length is due entirely to this cause. We are, however, safe in saying that there is no evidence that $1/\gamma$ *increases* as λ decreases, *i. e., there is no evidence that electrons with large initial velocities retain their ability to escape over longer paths than the slower electrons.*

This result is rather surprising and is of considerable importance, for it proves that an electron loses its ability to escape at a single catastrophe, and not by gradual process or a succession of small energy losses. If we define one of these catastrophes as a "collision," then we may identify $1/\gamma$ with the "mean free path" of the electron in the metal. This "mean free path" is apparently independent of the velocity of the electron, within the limits of velocity of photoelectrons. It is not easy to see how the theory of free electrons moving like molecules of a perfect gas in a metal can be reconciled with these results which indicate definite collisions of an inelastic type. These experiments are therefore consistent

[1] Compton and Richardson, Phil. Mag., 26, p. 549, 1913.

with the facts of specific heats of metals in indicating that electrons cannot exist in metals freely and independently sharing the thermal energy with the atoms.

The magnitude of the mean free path $1/\gamma$ is 2.67 $(10)^{-7}$ cm., which is greater than, but of the same order of magnitude as the distance between atomic centers in platinum. It is therefore probable that the electrons lose at least the greater part of their kinetic energy at encounters with atoms, and they may entirely lose their freedom at these encounters.

Patterson[1] has calculated the mean free path of conducting electrons by data regarding the Hall effect in platinum and also by applying J. J. Thomson's theory of the resistance of thin films. By each method he finds the mean free path to be about $6(10)^{-7}$ cm., not far different from the value we have calculated. Strict comparison is inadmissible, however, because the "mean free path" does not mean quite the same thing in the two cases, and because the assumptions underlying the formulæ used by Patterson cannot be accepted in their present form.

GOLD FILMS. In dealing with gold films the experimental difficulties were so great as to preclude the possibility of any great accuracy, and no extensive tests were made. The difficulties arise from the high resistence of films of the thickness necessary for the present tests, and are apparently due to lack of continuity of the films. Isolated portions of the films quickly charge up to retarding potentials, causing the rate of electrometer deflection to decrease rapidly. This phenomenon was noticed with only the very thinnest films of platinum.

In order to be more independent of errors from this cause, the films were kept shielded from light until the electrometer key was opened and we were ready to make an observation. A shutter was opened, so as to expose the film for two seconds. The deflection due to the electrons liberated in this interval was taken to represent the relative photoelectric sensitiveness of the film. The results of these tests are shown in Fig. 11. There is no evidence of a double maximum, though the determinations may not be accurate enough to make this conclusion certain. The mean free path $1/\gamma$ may be calculated by Fig. 4 to be about 5.0 $(10)^{-7}$ cm. The value of α used in this calculation is given by Meier[2] as $\alpha = .056\ \mu\mu^{-1}$ for wave-length 253.6 $\mu\mu$. Patterson has suggested a value $16(10)^{-7}$ cm. for the mean free path of the conducting electrons, while Partzsch and Hallwachs suggest

$$\frac{1}{\beta} = 11.6(10)^{-7} \text{ cm.}$$

(See the second assumption of the present paper.)

[1] Phil. Mag., 3, p. 655, 1902.

[2] *Loc. cit.*

SUMMARY.—The experiments described in this paper indicate that:

1. Photoelectrons, excited within a metal, lose their initial kinetic energy as the result of single and definite catastrophes, or "collisions," rather than by a gradual process or a succession of small energy losses.

2. The average distance which an electron can move before it loses its

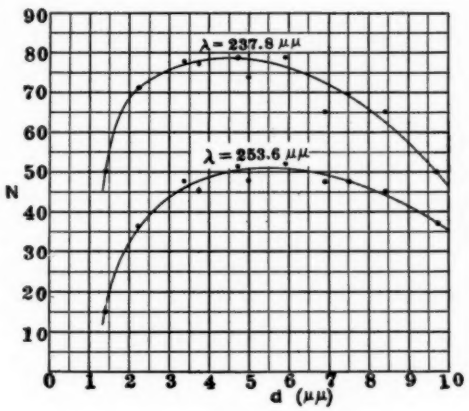

Fig. 11.

energy by one of these "collisions" is independent of the initial velocity and is of the same order as, but slightly larger than, the distance between atoms. The measurements indicate a mean free path of about 2.67 $(10)^{-7}$ cm. in platinum and 5.0 $(10)^{-7}$ cm. in gold.

3. Platinum films thinner than 2 $\mu\mu$ and gold films thinner than about 8 $\mu\mu$ are apt to be imperfectly conducting due to isolated regions which are not in conducting contact with the main body of the film. Platinum films therefore appear to be more homogeneous than gold films.

4. The small penetrating power of photo-electrons renders it extremely improbable that the thermionic emission from metals may be accounted for by considering it to be a photoelectric effect from the entire body of the metal integrated over the complete radiation spectrum.[1]

[1] This possibility is discussed in detail in Richardson's "The Emission of Electricity from Hot Bodies," pp. 95–102.

[2] Since the above paper was written, a paper dealing with the same general subject has been published in the February number of this Journal by Dr. Otto Stuhlman, Jr. His experimental results are not in good agreement with those in this paper, and his interpretation of them is quite different. We are at present unable to suggest a satisfactory explanation of the apparent lack of agreement.

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NEW BOOKS.

The Fundamental Equations of Dynamics and its Main Coördinate Systems Vectorially Treated and Illustrated from Rigid Dynamics. By FREDERICK SLATE. Berkeley: University of California Press, 1918. Pp. vii + 233.

This is a critical exposition of dynamical principles in the form of a commentary rather than a text-book or treatise, covering the concepts associated with systems of particles and rigid bodies with some passing reference to deformable media. One declared purpose is to utilize the values that appear in some of the more recent aspects of the subject, especially the point of view of energetics, the theory of relativity, and the formulation in terms of vector algebra. Mention is made of the Einstein theory, but the only relativity actually considered is of the Galileo-Newton type, extended to cover the study of motion relative to rotating frames of reference and the forces of Coriolis. Extended treatment is given the Euler coördinates for a rigid body, which also supplies the main illustration given of the Lagrange equations. At the end of the volume are a series of notes, partly historical, partly on comparison references. The style is somewhat verbose and seems stilted at times, perhaps because of a conscious effort at sufficient novelty of wording to avoid the risk of conventionalism which is so real in such a familiar subject. For this reason and in view of its apparent purpose the value of the book will appear best to those who already have acquaintance with the matter and are interested to think through its foundations in a fresh way.

A. C. L.